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TERMINAL (ENTER 1, 2, 3, OR ?):2

```
* * * * * * * * * *
                     Welcome to STN International
                 Web Page for STN Seminar Schedule - N. America
NEWS
NEWS
         DEC 01
                 ChemPort single article sales feature unavailable
NEWS
         FEB 02
                 Simultaneous left and right truncation (SLART) added
                 for CERAB, COMPUAB, ELCOM, and SOLIDSTATE
                 GENBANK enhanced with SET PLURALS and SET SPELLING
NEWS
         FEB 02
NEWS
         FEB 06
                 Patent sequence location (PSL) data added to USGENE
NEWS
         FEB 10 COMPENDEX reloaded and enhanced
      7
                 WTEXTILES reloaded and enhanced
NEWS
         FEB 11
     8 FEB 19
                 New patent-examiner citations in 300,000 CA/CAplus
NEWS
                 patent records provide insights into related prior
                 art.
NEWS
      9
         FEB 19
                 Increase the precision of your patent queries -- use
                 terms from the IPC Thesaurus, Version 2009.01
         FEB 23
                 Several formats for image display and print options
NEWS 10
                 discontinued in USPATFULL and USPAT2
NEWS 11
         FEB 23
                 MEDLINE now offers more precise author group fields
                 and 2009 MeSH terms
NEWS 12
         FEB 23
                 TOXCENTER updates mirror those of MEDLINE - more
                 precise author group fields and 2009 MeSH terms
NEWS 13
         FEB 23
                 Three million new patent records blast AEROSPACE into
                 STN patent clusters
         FEB 25
                 USGENE enhanced with patent family and legal status
NEWS 14
                 display data from INPADOCDB
NEWS 15
         MAR 06
                 INPADOCDB and INPAFAMDB enhanced with new display
                 formats
NEWS 16
         MAR 11
                 EPFULL backfile enhanced with additional full-text
                 applications and grants
                 ESBIOBASE reloaded and enhanced
NEWS 17
         MAR 11
                 CAS databases on STN enhanced with new super role
NEWS 18
         MAR 20
                 for nanomaterial substances
NEWS 19
         MAR 23
                 CA/CAplus enhanced with more than 250,000 patent
                 equivalents from China
NEWS 20
         MAR 30
                 IMSPATENTS reloaded and enhanced
NEWS 21
         APR 03
                 CAS coverage of exemplified prophetic substances
                 enhanced
NEWS 22
         APR 07
                 STN is raising the limits on saved answers
NEWS 23
         APR 24
                 CA/CAplus now has more comprehensive patent assignee
                 information
NEWS 24
         APR 26
                 USPATFULL and USPAT2 enhanced with patent
                 assignment/reassignment information
NEWS 25
         APR 28 CAS patent authority coverage expanded
```

NEWS 26 APR 28 ENCOMPLIT/ENCOMPLIT2 search fields enhanced NEWS 27 APR 28 Limits doubled for structure searching in CAS REGISTRY

NEWS 28 MAY 08 STN Express, Version 8.4, now available

NEWS EXPRESS MAY 08 09 CURRENT WINDOWS VERSION IS V8.4, AND CURRENT DISCOVER FILE IS DATED 06 APRIL 2009.

NEWS HOURS STN Operating Hours Plus Help Desk Availability NEWS LOGIN Welcome Banner and News Items

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FILE 'HOME' ENTERED AT 19:15:35 ON 10 MAY 2009

=> file reg
COST IN U.S. DOLLARS

SINCE FILE TOTAL ENTRY SESSION 0.22 0.22

FULL ESTIMATED COST

FILE 'REGISTRY' ENTERED AT 19:16:01 ON 10 MAY 2009
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STRUCTURE FILE UPDATES: 8 MAY 2009 HIGHEST RN 1144618-76-7 DICTIONARY FILE UPDATES: 8 MAY 2009 HIGHEST RN 1144618-76-7

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH January 9, 2009.

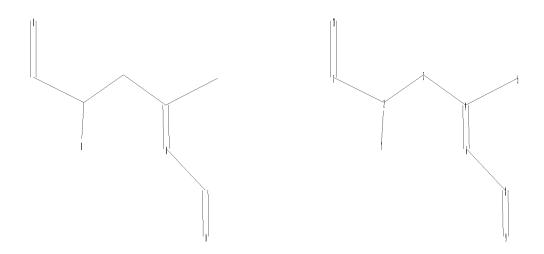
Please note that search-term pricing does apply when conducting  ${\tt SmartSELECT}$  searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

http://www.cas.org/support/stngen/stndoc/properties.html

=>

Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 2.str

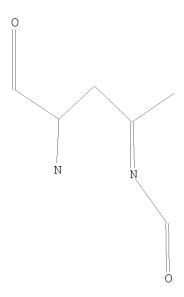


chain nodes :
1 2 3 4 5 6 7 8 9 10
chain bonds :
1-10 1-2 2-3 2-7 3-4 4-5 4-6 6-8 8-9
exact/norm bonds :
1-10 2-7 4-6 6-8 8-9
exact bonds :
1-2 2-3 3-4 4-5

Match level:
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 6:CLASS 7:CLASS 8:CLASS 9:CLASS 10:CLASS

## L1 STRUCTURE UPLOADED

=> d L1 HAS NO ANSWERS L1 STR



Structure attributes must be viewed using STN Express query preparation.

0 ANSWERS

=> 11

SAMPLE SEARCH INITIATED 19:16:13 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 17626 TO ITERATE

11.3% PROCESSED 2000 ITERATIONS INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*
BATCH \*\*COMPLETE\*\*
PROJECTED ITERATIONS: 344568 TO 360472
PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> 11 full

FULL SEARCH INITIATED 19:16:17 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 355951 TO ITERATE

100.0% PROCESSED 355951 ITERATIONS 0 ANSWERS SEARCH TIME: 00.00.05

L3 0 SEA SSS FUL L1

=> log h

COST IN U.S. DOLLARS
SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST 185.88 186.10

SESSION WILL BE HELD FOR 120 MINUTES
STN INTERNATIONAL SESSION SUSPENDED AT 19:16:40 ON 10 MAY 2009

Connecting via Winsock to STN

Welcome to STN International! Enter x:x

LOGINID: SSPTAJRK1626

PASSWORD:

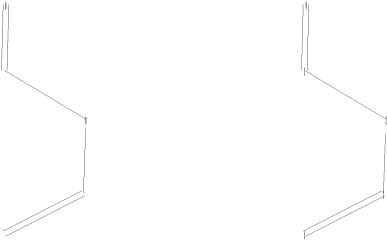
\* \* \* \* \* RECONNECTED TO STN INTERNATIONAL \* \* \* \* \* \* \* SESSION RESUMED IN FILE 'REGISTRY' AT 19:34:54 ON 10 MAY 2009 FILE 'REGISTRY' ENTERED AT 19:34:54 ON 10 MAY 2009 COPYRIGHT (C) 2009 American Chemical Society (ACS)

COST IN U.S. DOLLARS

SINCE FILE TOTAL ENTRY SESSION 185.88 186.10

FULL ESTIMATED COST

Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 3.str



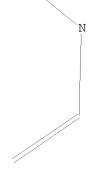
chain nodes :
1 2 3 4 5
chain bonds :
1-2 1-4 2-3 3-5
exact/norm bonds :
1-2 1-4 2-3
exact bonds :
3-5

Match level:
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS

L4 STRUCTURE UPLOADED

10587075.trn

=> d L4 HAS NO ANSWERS L4 STR



Structure attributes must be viewed using STN Express query preparation.

50 ANSWERS

=> 14

SAMPLE SEARCH INITIATED 19:35:27 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 39040 TO ITERATE

5.1% PROCESSED 2000 ITERATIONS INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 768988 TO 792612

PROJECTED ANSWERS: 109469 TO 118523

L5 50 SEA SSS SAM L4

=> 14 full

FULL SEARCH INITIATED 19:35:30 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 785185 TO ITERATE

100.0% PROCESSED 785185 ITERATIONS 110354 ANSWERS SEARCH TIME: 00.00.06

L6 110354 SEA SSS FUL L4

=>

Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 4.str

chain nodes : chain bonds : exact/norm bonds : 1 - 2Match level : 1:CLASS 2:CLASS L7 STRUCTURE UPLOADED => dL7 HAS NO ANSWERS Structure attributes must be viewed using STN Express query preparation. => 17 SAMPLE SEARCH INITIATED 19:35:51 FILE 'REGISTRY' SAMPLE SCREEN SEARCH COMPLETED - 1874427 TO ITERATE 2000 ITERATIONS 50 ANSWERS 0.1% PROCESSED INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED) SEARCH TIME: 00.00.01 FULL FILE PROJECTIONS: ONLINE \*\*INCOMPLETE\*\* BATCH \*\*INCOMPLETE\*\* 37422142 TO 37554938 PROJECTED ITERATIONS: 17118752 TO 17220736 PROJECTED ANSWERS: L8 50 SEA SSS SAM L7 Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 5.str

chain nodes :
1 2 3
chain bonds :

10587075.trn

## Page 8

1-2 1-3

exact/norm bonds :

1-2

exact bonds :

1 - 3

Match level:

1:CLASS 2:CLASS 3:CLASS

L9 STRUCTURE UPLOADED

=> d

L9 HAS NO ANSWERS

L9 STR



Structure attributes must be viewed using STN Express query preparation.

50 ANSWERS

=> 19

SAMPLE SEARCH INITIATED 19:36:28 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 1853194 TO ITERATE

0.1% PROCESSED 2000 ITERATIONS

INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*INCOMPLETE\*\*

BATCH \*\*INCOMPLETE\*\*

PROJECTED ITERATIONS: 36997661 TO 37130099

PROJECTED ANSWERS: 9245416 TO 9323588

L10 50 SEA SSS SAM L9

=>

Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 6.str



chain nodes :
1 2 3 4
chain bonds :

10587075.trn

Page 9

1-2 1-3 3-4 exact/norm bonds : 1-2 3-4 exact bonds :

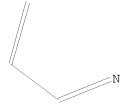
1 - 3

Match level:

1:CLASS 2:CLASS 3:CLASS 4:CLASS

L11 STRUCTURE UPLOADED

=> d L11 HAS NO ANSWERS L11 STR



Structure attributes must be viewed using STN Express query preparation.

50 ANSWERS

=> 111

SAMPLE SEARCH INITIATED 19:37:02 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 495814 TO ITERATE

0.4% PROCESSED 2000 ITERATIONS INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*INCOMPLETE\*\* BATCH \*\*INCOMPLETE\*\* PROJECTED ITERATIONS: 9876015 TO 9956545 PROJECTED ANSWERS: 344080 TO 359974

L12 50 SEA SSS SAM L11

=>

Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 7.str

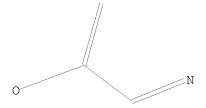
chain nodes :
1 2 3 4 5
chain bonds :
1-2 1-3 3-4 3-5
exact/norm bonds :
1-2 3-4 3-5
exact bonds :
1-3

Match level :

1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS

L13 STRUCTURE UPLOADED

=> d L13 HAS NO ANSWERS L13 STR



Structure attributes must be viewed using STN Express query preparation.

=> 113 SAMPLE SEARCH INITIATED 19:37:35 FILE 'REGISTRY' SAMPLE SCREEN SEARCH COMPLETED - 201443 TO ITERATE

1.0% PROCESSED 2000 ITERATIONS INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED) SEARCH TIME: 00.00.01

50 ANSWERS

FULL FILE PROJECTIONS: ONLINE \*\*INCOMPLETE\*\*

BATCH \*\*INCOMPLETE\*\*

PROJECTED ITERATIONS: 4002437 TO 4055283

PROJECTED ANSWERS: 110279 TO 119365

L14 50 SEA SSS SAM L13

=>

Uploading C:\Program Files\Stnexp\Queries\10587075\Struc 8.str



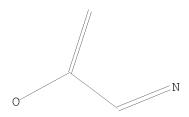


chain nodes:
1 2 3 4 5
chain bonds:
1-2 1-3 3-4 3-5
exact/norm bonds:
1-2 3-4 3-5
exact bonds:
1-3

Match level :
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS

L15 STRUCTURE UPLOADED

=> d L15 HAS NO ANSWERS L15 STR



Structure attributes must be viewed using STN Express query preparation.

=> d scan 114

L14 50 ANSWERS REGISTRY COPYRIGHT 2009 ACS on STN IN INDEX NAME NOT YET ASSIGNED
MF C21 H22 C12 N2 O5

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):0

=> file reg
COST IN U.S. DOLLARS

SINCE FILE TOTAL ENTRY SESSION 375.12 375.34

FULL ESTIMATED COST

FILE 'REGISTRY' ENTERED AT 19:39:39 ON 10 MAY 2009
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STRUCTURE FILE UPDATES: 8 MAY 2009 HIGHEST RN 1144618-76-7 DICTIONARY FILE UPDATES: 8 MAY 2009 HIGHEST RN 1144618-76-7

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http://www.cas.org/support/stngen/stndoc/properties.html

=> 16 and copper 372067 COPPER L16 12 L6 AND COPPER

=> d ibib abs hitstr 1-12
'IBIB' IS NOT A VALID FORMAT FOR FILE 'REGISTRY'

'ABS' IS NOT A VALID FORMAT FOR FILE 'REGISTRY' 'HITSTR' IS NOT A VALID FORMAT FOR FILE 'REGISTRY'

The following are valid formats:

Substance information can be displayed by requesting individual fields or predefined formats. The predefined substance formats are: (RN = CAS Registry Number)

REG – RN

SAM - Index Name, MF, and structure - no RN FIDE - All substance data, except sequence data

IDE - FIDE, but only 50 names
SQIDE - IDE, plus sequence data

SQIDE3 - Same as SQIDE, but 3-letter amino acid codes are used

SQD - Protein sequence data, includes RN

SQD3 - Same as SQD, but 3-letter amino acid codes are used

SQN - Protein sequence name information, includes RN

EPROP - Table of experimental properties
PPROP - Table of predicted properties
PROP - EPROP, ETAG, PPROP and SPEC

Any CA File format may be combined with any substance format to obtain CA references citing the substance. The substance formats must be cited first. The CA File predefined formats are:

ABS -- Abstract

APPS -- Application and Priority Information

BIB -- CA Accession Number, plus Bibliographic Data

CAN -- CA Accession Number

CBIB -- CA Accession Number, plus Bibliographic Data (compressed)

IND -- Index Data

IPC -- International Patent Classification

PATS -- PI, SO

STD -- BIB, IPC, and NCL

IABS -- ABS, indented, with text labels IBIB -- BIB, indented, with text labels

ISTD -- STD format, indented

OBIB ----- AN, plus Bibliographic Data (original) OIBIB ----- OBIB, indented with text labels

SBIB ----- BIB, no citations SIBIB ----- IBIB, no citations

The ALL format gives FIDE BIB ABS IND RE, plus sequence data when it is available.

The MAX format is the same as ALL.

The IALL format is the same as ALL with BIB ABS and IND indented, with text labels.

For additional information, please consult the following help messages:

HELP DFIELDS -- To see a complete list of individual display fields.

11

12

RN

RN

HELP FORMATS -- To see detailed descriptions of the predefined formats. ENTER DISPLAY FORMAT (IDE):

ENTER DISPLAY FORMAT (IDE):req 84518-21-8 REGISTRY 1 RN 2 RN 84433-35-2 REGISTRY 3 RN 84433-34-1 REGISTRY 4 RN 63986-67-4 REGISTRY 5 RN 58850-31-0 REGISTRY 6 RN 24761-97-5 REGISTRY 7 RN 21437-34-3 REGISTRY 8 RN 20704-23-8 REGISTRY 9 RN 20704-22-7 REGISTRY 10 RN 20704-21-6 REGISTRY

=> file caplus
COST IN U.S. DOLLARS
SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST
8.83 384.17

18498-00-5 REGISTRY

1865-27-6 REGISTRY

FILE 'CAPLUS' ENTERED AT 19:40:18 ON 10 MAY 2009
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FILE COVERS 1907 - 10 May 2009 VOL 150 ISS 20
FILE LAST UPDATED: 8 May 2009 (20090508/ED)
REVISED CLASS FIELDS (/NCL) LAST RELOADED: Feb 2009
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Feb 2009

CAplus now includes complete International Patent Classification (IPC) reclassification data for the third quarter of 2008.

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http://www.cas.org/legal/infopolicy.html

This file contains CAS Registry Numbers for easy and accurate

=> 16 and copper 23077 L6 1042804 COPPER L17 406 L6 AND COPPER

#### Page 15

 $\Rightarrow$  117 and imin?

100576 IMIN?

L18 26 L17 AND IMIN?

=> d ibib abs hitstr 1-26

L18 ANSWER 1 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2007:532529 CAPLUS

DOCUMENT NUMBER: 147:143304

TITLE: Synthesis of substituted pyridines and quinolines

AUTHOR(S): Hill, Matthew D.; Movassaghi, Mohammad

CORPORATE SOURCE: Department of Chemistry, Massachusetts Institute of

Technology, Cambridge, MA, 02139, USA

SOURCE: Synthesis (2007), (7), 1115-1119

CODEN: SYNTBF; ISSN: 0039-7881

PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 147:143304

AB A variety of N-vinyl and N-aryl amides were converted to the corresponding pyridine and quinoline derivs., resp. Amide activation and nucleophilic

addition of copper(I) (trimethylsilyl)acetylide efficiently provided the desired alkynyl imines. Ruthenium-catalyzed protodesilylation and cycloisomerization of these imines gave the corresponding aza heterocycles.

IT 49747-42-4 860723-95-1 887236-62-6

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of pyridines and quinolines by addition of copper silylacetylide to N-vinyl and N-aryl amides, ruthenium-catalyzed

protodesilylation, and cycloisomerization)

RN 49747-42-4 CAPLUS

CN Benzamide, N-(2-phenylethenyl)- (CA INDEX NAME)

RN 860723-95-1 CAPLUS

CN Benzamide, N-[2-(3,4-dimethoxyphenyl)ethenyl]- (CA INDEX NAME)

RN 887236-62-6 CAPLUS

CN Benzamide, N-[2-(1-naphthalenyl)ethenyl]- (CA INDEX NAME)

REFERENCE COUNT: 39 THERE ARE 39 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 2 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:1336881 CAPLUS

DOCUMENT NUMBER: 146:251557

TITLE: Catalytic asymmetric amination of enecarbamates

AUTHOR(S): Matsubara, Ryosuke; Kobayashi, Shu

CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, University

of Tokyo, Tokyo, 113-0033, Japan

SOURCE: Angewandte Chemie, International Edition (2006),

45(47), 7993-7995

CODEN: ACIEF5; ISSN: 1433-7851 Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:251557

GΙ

PUBLISHER:

## \* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB Azodicarboxylates I (R = i-Pr, Me, Et, Bn) react with various enecarbamates, e.g. II, derived from aromatic and aliphatic ketones and aldehydes, via copper-catalyzed asym. amination, to provide acylimines, e.g. III, ketones, e.g. IV, and diamines, e.g. V, in good yields with high enantioselectivity. The catalyst loading necessary for high enantioselectivity was generally low, with 0.2 mol% catalyst sufficient in some cases. The transition-state model was also discussed in order to explain the stereoselectivity.

IT 260967-14-4 750596-67-9 750596-68-0

750596-69-1 750596-71-5

RL: RCT (Reactant); RACT (Reactant or reagent)

(asym. synthesis of acylimines, ketones and diamines via copper -catalyzed asym. amination of enecarbamates with azodicarboxylates)

RN 260967-14-4 CAPLUS

CN Carbamic acid, N-(1E)-1-propen-1-yl-, phenylmethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} E & H \\ N & O \end{array} \begin{array}{c} Ph \\ O \end{array}$$

# Page 17

RN 750596-67-9 CAPLUS

CN Carbamic acid, N-[(1E)-1-phenyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

$$\begin{array}{c|c} O & Ph \\ \hline Ph & & E \\ \hline Ph & & H \end{array}$$

RN 750596-68-0 CAPLUS

CN Carbamic acid, N-[(1Z)-1-phenyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-69-1 CAPLUS

CN Carbamic acid, N-[(1E)-1-(4-methoxyphenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-71-5 CAPLUS

CN Carbamic acid, N-[(1E)-1-(4-chlorophenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

TT 79152-68-4P 750596-75-9P 925670-22-0P 925670-23-1P 925670-24-2P 925670-25-3P

925670-26-4P 925670-27-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(asym. synthesis of acylimines, ketones and diamines via copper -catalyzed asym. amination of enecarbamates with azodicarboxylates)

RN 79152-68-4 CAPLUS

CN Carbamic acid, N-[(1E)-1-phenyl-1-propen-1-yl]-, methyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-75-9 CAPLUS

CN Carbamic acid, N-[(1E)-1-ethyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 925670-22-0 CAPLUS

CN Carbamic acid, N-[(1E)-1-phenyl-1-propen-1-yl]-, ethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} O & Ph \\ \hline E & Me \\ \hline N & H \end{array}$$

RN 925670-23-1 CAPLUS

CN Carbamic acid, N-[(1E)-1-phenyl-1-propen-1-yl]-, 2-propen-1-yl ester (CA INDEX NAME)

Double bond geometry as shown.

$$H_2C$$
 $O$ 
 $H$ 
 $E$ 
 $Me$ 
 $O$ 
 $Ph$ 

RN 925670-24-2 CAPLUS

CN Carbamic acid, N-[(1E)-1-(2-methylphenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 925670-25-3 CAPLUS

CN Carbamic acid, N-[(1E)-1-(3-methylphenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

RN 925670-26-4 CAPLUS

CN Carbamic acid, N-[(1E)-1-(4-methylphenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 925670-27-5 CAPLUS

CN Carbamic acid, N-[(1E)-1-methyl-1-buten-1-yl]-, phenylmethyl ester INDEX NAME)

Double bond geometry as shown.

THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS REFERENCE COUNT: 31 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

CAPLUS COPYRIGHT 2009 ACS on STN L18 ANSWER 3 OF 26

ACCESSION NUMBER: 2006:1079247 CAPLUS

DOCUMENT NUMBER: 146:8035

TITLE: High turnover frequency observed in catalytic

enantioselective additions of enecarbamates and

enamides to iminophosphonates

AUTHOR(S): Kiyohara, Hiroshi; Matsubara, Ryosuke; Kobayashi, Shu CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, University

of Tokyo, Tokyo, Japan

SOURCE: Organic Letters (2006), 8(23), 5333-5335

CODEN: ORLEF7; ISSN: 1523-7060

American Chemical Society PUBLISHER:

DOCUMENT TYPE: Journal LANGUAGE: English

CASREACT 146:8035 OTHER SOURCE(S):

Chiral  $\alpha$ -aminophosphonates were prepared by copper /diamine-catalyzed asym. addition fo enamides to iminomethylphosphonates. Reaction of (EtO) 2POCH:NX (1, X =2,2,2-trichloroethoxycarbonyl, Troc) with CH2:C(Ar)NHCbz catalyzed by Cu(OTf)2/(R,R)-Ar1CH2NHCHPhCHPhNHCH2Ar1 (Ar1 = 1-naphthyl, Ph) afforded chiral  $\alpha$ -aminophosphonates (EtO)2P(O)CH(NHX)CH2COAr (4a-f, Ar = Ph, 4-MeC6H4, 4-ClC6H4, 2-naphthalenyl, 3-MeC6H4). In the addition reactions, extremely high turnover frequency of the catalyst was observed in comparison with that of silicon enolate addition reactions. This is presumably due to fast transfer of the proton that locates on the nucleophiles.

IT 697301-71-6 697301-72-7 697301-73-8

697301-74-9 697301-75-0 915748-71-9

915748-72-0

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of chiral  $\alpha-\text{aminophosphonates}$  by asym. addition of enamides with iminophosphonates catalyzed by copper-diamine

complexes)

RN 697301-71-6 CAPLUS

CN Carbamic acid, N-(1-phenylethenyl)-, phenylmethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} \mathsf{CH}_2 & \mathsf{O} \\ \parallel & \parallel \\ \mathsf{Ph} - \mathsf{C} - \mathsf{NH} - \mathsf{C} - \mathsf{O} - \mathsf{CH}_2 - \mathsf{Ph} \end{array}$$

RN 697301-72-7 CAPLUS

CN Carbamic acid, N-[1-(4-methoxyphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-73-8 CAPLUS

CN Carbamic acid, N-[1-(4-chlorophenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-74-9 CAPLUS

CN Carbamic acid, N-[1-(4-methylphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

## Page 22

RN 697301-75-0 CAPLUS

CN Carbamic acid, N-[1-(2-naphthalenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 915748-71-9 CAPLUS

CN Benzamide, N-[1-(4-chlorophenyl)ethenyl]- (CA INDEX NAME)

RN 915748-72-0 CAPLUS

CN Benzamide, N-[1-(3-methylphenyl)ethenyl]- (CA INDEX NAME)

IT 857489-17-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of chiral  $\alpha$ -aminophosphonates by asym. addition of enamides with iminophosphonates catalyzed by copper-diamine complexes)

RN 857489-17-9 CAPLUS

CN Benzamide, N-(1-phenylethenyl) - (CA INDEX NAME)

$$\begin{array}{c|c} \text{CH}_2 & \text{O} \\ \parallel & \parallel \\ \text{Ph-} \text{C--NH--C--Ph} \end{array}$$

REFERENCE COUNT: 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 4 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:984204 CAPLUS

#### Page 23

DOCUMENT NUMBER: 145:505113

TITLE: Ene Carbamates as Imine Surrogates:

Nucleophilic Addition of 1,3-Dicarbonyl Compounds to

Ene Carbamates

AUTHOR(S): Kobayashi, Shu; Gustafsson, Tomas; Shimizu, Yusuke;

Kiyohara, Hiroshi; Matsubara, Ryosuke

CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, University

of Tokyo, Tokyo, Japan

SOURCE: Organic Letters (2006), 8(21), 4923-4925

CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 145:505113

GΙ

AB Novel Mannich-type reactions of 1,3-dicarbonyl compds. with ene carbamates were developed. Thus, reaction of the oxocyclopentanecarboxylate I in 1,2-dichloroethane containing Cu(O2CCF3)2 with (Z)-PhCH2CH:CHNHCO2CH2Ph over 12 h gave 89% (oxocyclopentyl)phenylpropylcarbamate II. Stable and storable ene carbamates act as surrogates of aliphatic aldehyde-derived imines, which are known to be difficult to isolate and store.

IT 88425-24-5 260967-07-5 914396-43-3

914396-45-5 914396-48-8

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of (alkoxycarbonylamino)methyl dicarbonyl compds. via Mannich-type addition of ene carbamates to dicarbonyl compds.)

RN 88425-24-5 CAPLUS

CN Carbamic acid, N-[(1E)-2-phenylethenyl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 260967-07-5 CAPLUS

CN Carbamic acid, [(1Z)-3-phenyl-1-propenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

$$\begin{array}{c|c} Z & H \\ \hline N & O \\ \hline \end{array} \begin{array}{c} Ph \\ \hline \end{array}$$

RN 914396-43-3 CAPLUS

CN Carbamic acid, [(1Z)-3-phenyl-1-propenyl]-, 1,1-dimethylethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

$$t\text{-BuO} \xrightarrow[H]{O} Ph$$

RN 914396-45-5 CAPLUS

CN Carbamic acid, [(1Z)-3-methyl-1-butenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 914396-48-8 CAPLUS

CN Carbamic acid, [(1E)-3-methyl-1-butenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 5 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:787790 CAPLUS

DOCUMENT NUMBER: 145:230417

TITLE: Preparation of  $\delta$ - iminomalonic acid

esters as  $\delta$ -substituted carboxylic acids with

chiral copper catalysts

INVENTOR(S): Kobayashi, Shu; Kawai, Nobuyuki

PATENT ASSIGNEE(S): Japan Science and Technology Agency, Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 19 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2006206550	А	20060810	JP 2005-24534 JP 2005-24534	20050131
PRIORITY APPLN. INFO.:			JP 2005-24554	20030131

OTHER SOURCE(S): MARPAT 145:230417

Title esters are prepared by treatment of enecarbamates with alkylidene malonate esters in the presence of Cu catalysts. Thus, PhCH2O2CNHCPh:CH2 was treated with MeCH:C(CO2Ph)2 and Cu catalyst [prepared from Cu(OTf)2 and trans-ZNHCHPhCHPhNHZ (Z =  $\beta$ -naphthylmethyl)] and the resulting imine was hydrolyzed to give 98% PhCOCH2CHMeCH(CO2Ph)2 with 76% ee.

IT 697301-71-6

RL: RCT (Reactant); RACT (Reactant or reagent) (preparation of optically active  $\delta$ -substituted carboxylic acids by Michael addition via iminomalonates)

RN 697301-71-6 CAPLUS

CN Carbamic acid, N-(1-phenylethenyl)-, phenylmethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} \mathtt{CH_2} & \mathtt{O} \\ \parallel & \parallel \\ \mathtt{Ph-C-NH-C-O-CH_2-Ph} \end{array}$$

L18 ANSWER 6 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:787692 CAPLUS

DOCUMENT NUMBER: 145:230421

TITLE: Enantioselective nucleophilic addition of enamides to

azo compounds Kobayashi, Shu

PATENT ASSIGNEE(S): Japan Science and Technology Agency, Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 20 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

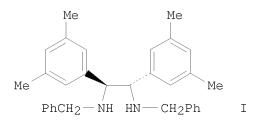
PATENT INFORMATION:

INVENTOR(S):

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE		
JP 2006206554	A	20060810	JP 2005-24614	20050131		
PRIORITY APPLN. INFO.:			JP 2005-24614	20050131		
OTHER SOURCE (S) .	маррат	1/5 • 230/21				

OTHER SOURCE(S): MARPAT 145:230421

GΙ



AB Optically active iminohydrazines are prepared by nucleophilic addition of enamides to N:N groups of azo compds. in the presence of chiral Cu catalysts. Optically active ketohydrazines, (acylamino)hydrazines, and diamines are prepared from the iminohydrazines. Thus, iso-PrO2CN:NCO2-iso-Pr was treated with MeCH:CPhNHCO2CH2Ph in the presence of catalyst solution prepared from I and Cu(OTf)2 in MePh to give 96% I with 97% ee.

IT 750596-67-9 750596-68-0

RL: RCT (Reactant); RACT (Reactant or reagent)

(enantioselective nucleophilic addition of enamides to azo compds. with chiral Cu catalysts)

RN 750596-67-9 CAPLUS

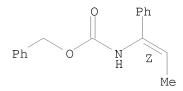
CN Carbamic acid, N-[(1E)-1-phenyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-68-0 CAPLUS

CN Carbamic acid, N-[(1Z)-1-phenyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.



L18 ANSWER 7 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:333966 CAPLUS

DOCUMENT NUMBER: 145:27389

TITLE: General Approach to the Coupling of Organoindium

Reagents with Imines via Copper

Page 27

Catalysis

AUTHOR(S): Black, Daniel A.; Arndtsen, Bruce A.

CORPORATE SOURCE: Department of Chemistry, McGill University, Montreal,

QC, H3A 2K6, Can.

SOURCE: Organic Letters (2006), 8(10), 1991-1993

CODEN: ORLEF7; ISSN: 1523-7060

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 145:27389

AB A copper-catalyzed three-component coupling of organoindium reagents with imines and acid chlorides is described. This mild carbon-carbon bond forming reaction requires only one-third of an equivalent of indium reagent to proceed in high yield, with the sole byproduct being indium trichloride. The reaction demonstrates broad generality, with aryl-, heteroaryl-, vinyl-, and alkylindiums, as well as functionalized imines and acid chlorides, all providing  $\alpha$ -substituted amides or N-protected amines in a single step.

IT 858126-59-7P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of amines by copper-catalyzed three-component coupling of organoindium reagents with imines and acid chlorides)

RN 858126-59-7 CAPLUS

CN Benzamide, N-ethyl-4-methyl-N-(3-phenyl-1,4-pentadien-1-yl)- (CA INDEX NAME)

REFERENCE COUNT: 53 THERE ARE 53 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 8 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:266204 CAPLUS

DOCUMENT NUMBER: 144:488547

TITLE: Synthesis of Substituted Pyridine Derivatives via the

Ruthenium-Catalyzed Cycloisomerization of

3-Azadienynes

AUTHOR(S): Movassaghi, Mohammad; Hill, Matthew D.

CORPORATE SOURCE: Department of Chemistry, Massachusetts Institute of

Technology, Cambridge, MA, 02139, USA

SOURCE: Journal of the American Chemical Society (2006),

128(14), 4592-4593

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:488547

GΙ

AB A two-step conversion of various N-vinyl and N-aryl amides, e.g. I (R1, R3 = H, MeO; R2 = H, F3C), to the corresponding substituted pyridines and quinolines, e.g. II, resp., is described. The process involves the direct conversion of amides, including sensitive N-vinyl amides, to the corresponding trimethylsilyl alkynyl imines, e.g. III, followed by a ruthenium-catalyzed protodesilylation and cycloisomerization. A wide range of new alkynyl imines are prepared and readily converted to the corresponding azaheterocycles.

IT 78007-47-3 860723-95-1 887236-62-6

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of substituted and heterocycle-fused pyridines and quinolines via coupling of aromatic amides with copper acetylide and ruthenium-catalyzed cycloisomerization of azadienynes)

RN 78007-47-3 CAPLUS

CN Benzamide, N-[(1E)-2-phenylethenyl]- (CA INDEX NAME)

Double bond geometry as shown.

RN 860723-95-1 CAPLUS

CN Benzamide, N-[2-(3,4-dimethoxyphenyl)ethenyl]- (CA INDEX NAME)

RN 887236-62-6 CAPLUS

CN Benzamide, N-[2-(1-naphthalenyl)ethenyl]- (CA INDEX NAME)

REFERENCE COUNT: 71 THERE ARE 71 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 9 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2005:1211474 CAPLUS

DOCUMENT NUMBER: 143:460279

TITLE: Terpenoid-based cycloolefin diphosphine ligands for

transition metal catalyzed asymmetric reactions and a

process for preparation thereof

INVENTOR(S): Kadyrov, Renat; Almena Perea, Juan Jose; Monsees,

Axel; Riermeier, Thomas; Iladinov, Ilias

PATENT ASSIGNEE(S): Degussa A.-G., Germany SOURCE: Eur. Pat. Appl., 45 pp.

SOURCE: Eur. Pat. App. CODEN: EPXXDW

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.			KIND DATE			,	APPLICATION NO.					DATE						
EP 1595		BF		A1	A1 20051116 EP 2004-11152 DE, DK, ES, FR, GB, GR, IT, LI, LU,													
1(,									AL,								HR	
CA 2559	242			A1		2005	1117		CA 2	005-	2559.	242		2	0050	414		
WO 2005	10840	7		A1 200511			1117	WO 2005-EP3932						20050414				
W:	ΑE,	AG,	AL,	ΑM,	AT,	ΑU,	ΑZ,	BA,	BB,	BG,	BR,	BW,	BY,	BZ,	CA,	CH,		
	CN,	CO,	CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EC,	EE,	EG,	ES,	FΙ,	GB,	GD,		
	GE,	GH,	GM,	HR,	HU,	ID,	IL,	IN,	IS,	JP,	KE,	KG,	KM,	KP,	KR,	KΖ,		
	LC,	LK,	LR,	LS,	LT,	LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NA,		
	NI,	NO,	NZ,	OM,	PG,	PH,	PL,	PT,	RO,	RU,	SC,	SD,	SE,	SG,	SK,	SL,		
	SM, ZM,	•	TJ,	TM,	TN,	TR,	TT,	TZ,	UA,	UG,	US,	UZ,	VC,	VN,	YU,	ZA,		

GT

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RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
              AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,
              RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
              MR, NE, SN, TD, TG
     EP 1745058
                                   20070124
                                                EP 2005-731071
                            Α1
                                                                          20050414
         R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE,
              IS, IT, LI, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR
     CN 1946730
                                   20070411
                                                CN 2005-80012209
                            Α
     BR 2005011027
                                   20071127
                                                BR 2005-11027
                            Α
                                                                          20050414
     JP 2007537171
                            Τ
                                   20071220
                                                JP 2007-511911
                                                                          20050414
     US 20080306264
                            Α1
                                   20081211
                                                US 2006-579626
                                                                          20061106
     MX 2006012903
                                   20070126
                                                MX 2006-12903
                                                                          20061107
                            Α
     IN 2006KN03265
                                   20070608
                                                IN 2006-KN3265
                            Α
                                                                          20061108
                                   20070116
                                                KR 2006-723627
     KR 2007007923
                                                                          20061110
                            Α
PRIORITY APPLN. INFO.:
                                                EP 2004-11152
                                                                          20040511
                                                WO 2005-EP3932
                                                                          20050414
                                                                      W
OTHER SOURCE(S):
                          CASREACT 143:460279; MARPAT 143:460279
```

AΒ Chiral diphosphines I [ring Q1 = optionally unsatd. 4-8-membered(non)aromatic (azahetero)cycle or polycycle, ring Q2 = partially saturated non-aromatic 5-8-membered (poly)cyclic or heterocyclic moiety; both rings optionally substituted by aliphatic, aromatic or functional substituents; R1, R2, R3, R3 = alkyl, aryl, aralkyl, alkenyl, alkynyl, alkoxy, aryloxy alkylthio, (un)substituted (hetero)cyclyl; R1-R2 or R3-R4 = 3-8-membered (un) substituted (hetero) cyclyl, (hetero) aromatic moiety; phosphorus atoms optionally are chiral], useful as ligands for transition-metal-catalyzed asym. hydrogenation, alkylation, hydrosilylation, isomerization and other reactions, were prepared by reaction of protected organometallic derivs. of the ring Q1 with halogen derivs. of enol sulfonates, phosphates or carbamates of the ring Q2. In an example, 0.143 mol of (1R)-3-bromocamphor enol triflate was coupled with 4-bromo-2,5-dimethyl-3-thienylmagnesium bromide (prepared from 0.286 mol of 3,4-dibromothiophene in 250 mL of THF) in the presence of 7 mmol of Pd(PPh3)2Cl2 catalyst at 50° overnight to give II (X1 = X2 = Br). P(3,5-Me2C6H3)2; X1 = P(3,5-Me2C6H3)2, X2 = PPh2) were prepared by stepwise phosphination of II (X1 = X2 = Br); rhodium-catalyzed asym. hydrogenation

of di-Me itaconate gave di-Me (2S)-2-methylsuccinate with 92% ee.

IT 55065-02-6 57957-24-1 60676-51-9

67654-56-2 136744-85-9

RL: RCT (Reactant); RACT (Reactant or reagent)

(process for preparation of chiral cycloalkenyl diphosphines with terpenoid backbone as ligands for transition metal-catalyzed asym. hydrogenation)

RN 55065-02-6 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-phenyl-, (2Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 57957-24-1 CAPLUS

CN Acetamide, N-(1-phenylethenyl) - (CA INDEX NAME)

RN 60676-51-9 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-phenyl-, methyl ester, (2Z)- (CA INDEX NAME)

Double bond geometry as shown.

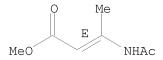
RN 67654-56-2 CAPLUS

CN 2-Butenoic acid, 3-(acetylamino)-, methyl ester, (2Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 136744-85-9 CAPLUS

CN 2-Butenoic acid, 3-(acetylamino)-, methyl ester, (2E)- (CA INDEX NAME)



REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 10 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2005:696867 CAPLUS

DOCUMENT NUMBER: 143:194235

TITLE: Method of enantio-selective nucleophilic addition

reaction for conversion of enamide to imine and method of synthesizing  $\alpha\text{--amino--}\gamma\text{--keto}$ 

acid ester

INVENTOR(S):
Kobayashi, Shu

PATENT ASSIGNEE(S): Japan Science and Technology Agency, Japan

SOURCE: PCT Int. Appl., 25 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

P <i>P</i>	PATENT NO.					KIND DATE				APPLICATION NO.						DATE		
WC	WO 2005070876			A1	_	2005	0804	WO 2005-JP1282						20050124				
	W: AE, AG, AL,		AL,	AM,	ΑT,	ΑU,	AZ,	BA,	BB,	BG,	BR,	BW,	BY,	BZ,	CA,	CH,		
		CN,	CO,	CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EC,	EE,	EG,	ES,	FΙ,	GB,	GD,	
		GE,	GH,	GM,	HR,	HU,	ID,	IL,	IN,	IS,	JP,	ΚE,	KG,	KP,	KR,	KΖ,	LC,	
		LK,	LR,	LS,	LT,	LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NA,	ΝI,	
		NO,	NZ,	OM,	PG,	PH,	PL,	PT,	RO,	RU,	SC,	SD,	SE,	SG,	SK,	SL,	SY,	
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			GM,	ΚE,	LS,	MW,	ΜZ,	NA,	SD,	SL,	SZ,	TZ,	UG,	ZM,	ZW,	ΑM,		
		ΑZ,	BY,	KG,	KΖ,	MD,	RU,	ТJ,	TM,	ΑT,	BE,	BG,	CH,	CY,	CZ,	DE,	DK,	
		EE,	ES,	FΙ,	FR,	GB,	GR,	HU,	ΙE,	IS,	ΙΤ,	LT,	LU,	MC,	NL,	PL,	PT,	
		RO,	SE,	SI,	SK,	TR,	BF,	ВJ,	CF,	CG,	CI,	CM,	GΑ,	GN,	GQ,	GW,	ML,	
		MR,	NE,	SN,	TD,	ΤG												
EF	EP 1707559				A1		2006	1004		EP 2005-704279					2005012			
	R:	DE,	FR,	GB														
US 20070161804			A1		20070712 US 2006-587075							2	0060	929				
PRIORITY APPLN. INFO.:								JP 2	004-	1640	7	-	A 2	0040	123			
										WO 2	005-	JP12	82	•	W 2	0050	124	
OTHER SOURCE(S): GI					MAR:	PAT	143:	1942	35									

- $^{\star}$  STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY AVAILABLE VIA OFFLINE PRINT  $^{\star}$
- AB An asym. synthesis of amino acid compound such as  $\alpha$ -amino- $\gamma$ -keto acid ester and  $\alpha, \gamma$ -diamino acid esters and conversion of the latter into  $\gamma$ -lactams are described. The amino acid compound is useful as a starting material or synthetic intermediate for production of

ΙT

RN CN

RN

CN

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medicinal products, agrochems., perfumes, functional polymers, etc. There
     is provided a method of enantio-selective nucleophilic addition reaction of
     enamide of formula R5R6C:C(R4)NHCOR3 [R3 = (un)substituted hydrocarbyl
     optionally having a substituent bonded through O; R4 = (un)substituted
     hydrocarbyl; R5, R6 = H, (un)substituted hydrocarbyl; at least one of R5
     and R6 is H] to imine compound of formula R102CCH:NR2 [R1 =
     (un) substituted hydrocarbyl; R2 = RCO, RO2C; wherein R = (un) substituted
     hydrocarbyl] in the presence of a chiral copper catalyst to give
     optically active \alpha-amino-\gamma- imino acid ester (I) or
     (II) (R1-R6 = same as above) with formation of chiral amino group. I and
     II are further converted into \alpha-amino-\gamma-keto acid ester (III)
     or (IV) by acid hydrolysis or into \alpha, \gamma-diamino acid ester (V)
     or (VI) by reduction Removing the acyl group of \gamma-amino group from the
     \alpha,\gamma-diamino acid ester V or VI followed by cyclization gives
     \gamma-lactams (VII) or (VIII). Thus, 7.2 mg Cu(OTf)2 was dried at
     100° for 2 h followed by adding 10.8 mg
     (1R, 2R) -1, 2-diphenyl-1, 2-bis(1-naphthylamino) ethane under Ar and hen 1.5
     mL CH2Cl2 and the light blue solution was stirred for \geq 2 h and cooled
     at 0^{\circ}. To the solution were added a solution of 0.30 mmol enamide (IX)
     in 0.8 mL CH2C12 and then slowly a solution of 0.20 mmol Et02CCH:NCOC11H23 in
     2.0 mL for 30 min. The resulting reaction was stirred at 0° for 15 \,
     min and quenched by adding saturated aqueous NaHCO3 to give 77%
     \alpha-amino-\gamma- imino acid (X) in a syn/anti ratio of
     86/14 with 94\% ee (syn).
     52820-12-9 72328-04-2 697301-71-6
     697301-72-7 697301-73-8 697301-75-0
     697301-76-1
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (asym. synthesis of \alpha-amino-\gamma-keto acid ester,
        \alpha, \gamma\text{-diamino} acid esters, and \gamma\text{-lactams} via
        enantioselective nucleophilic addition reaction of enamides to
        imines in presence of chiral copper complex)
     52820-12-9 CAPLUS
     Carbamic acid, N-(1-methylethenyl)-, ethyl ester (CA INDEX NAME)
           CH<sub>2</sub>
EtO-C-NH-C-Me
     72328-04-2 CAPLUS
```

RN 697301-71-6 CAPLUS Carbamic acid, N-(1-phenylethenyl)-, phenylmethyl ester (CA INDEX NAME) CN

Carbamic acid, N-(1-phenylethenyl)-, methyl ester (CA INDEX NAME)

$$\begin{array}{c|c} \mathsf{CH}_2 & \mathsf{O} \\ \parallel & \parallel \\ \mathsf{Ph} - \mathsf{C} - \mathsf{NH} - \mathsf{C} - \mathsf{O} - \mathsf{CH}_2 - \mathsf{Ph} \end{array}$$

RN 697301-72-7 CAPLUS

CN Carbamic acid, N-[1-(4-methoxyphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-73-8 CAPLUS

CN Carbamic acid, N-[1-(4-chlorophenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-75-0 CAPLUS

CN Carbamic acid, N-[1-(2-naphthalenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-76-1 CAPLUS

CN Carbamic acid, [(1E)-1-(4-methoxyphenyl)-1-propenyl]-, ethyl ester (9CI) (CA INDEX NAME)

REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 11 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2005:436084 CAPLUS

DOCUMENT NUMBER: 143:133559

TITLE: Copper-Catalyzed Cross-Coupling of

Imines, Acid Chlorides, and Organostannanes: A Multicomponent Synthesis of  $\alpha\text{--Substituted Amides}$ 

AUTHOR(S): Black, Daniel A.; Arndtsen, Bruce A.

CORPORATE SOURCE: Department of Chemistry, McGill University, Montreal,

QC, H3A 2K6, Can.

SOURCE: Journal of Organic Chemistry (2005), 70(13), 5133-5138

CODEN: JOCEAH; ISSN: 0022-3263

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:133559

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$$\begin{array}{c|c} & & \\ & N & \\ & & CH_2 \\ \hline & S & \\ \end{array}$$

AB A copper-catalyzed cross-coupling of organotin reagents with imines and acid chlorides is reported. The reaction proceeds efficiently with a range of vinyl-, alkyl-, aryl- and heteroaryl-substituted organostannanes as well as a diverse set of imines of non-enolizable aldehydes. Use of chloroformates also allows for the formation of N-protected  $\alpha-$  substituted amines. This chemical has been applied to the synthesis of isoquinoline alkaloid derivs. (e.g. I) through the activation of cyclic imines.

IT 858126-59-7P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of  $\alpha$ -substituted amides via copper-catalyzed cross-coupling of imines, acid chlorides and organostannanes)

RN 858126-59-7 CAPLUS

CN Benzamide, N-ethyl-4-methyl-N-(3-phenyl-1,4-pentadien-1-yl)- (CA INDEX NAME)

REFERENCE COUNT: 68 THERE ARE 68 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 12 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2004:559323 CAPLUS

DOCUMENT NUMBER: 141:243143

TITLE: Highly diastereo- and enantioselective reactions of

ene carbamates with ethyl glyoxylate to give optically

active syn and anti  $\alpha$ -alkyl- $\beta$ -hydroxy

imines and ketones

AUTHOR(S): Matsubara, Ryosuke; Nakamura, Yoshitaka; Kobayashi,

Shu

CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, The

University of Tokyo, Hongo, Bunkyo-ku, Tokyo,

113-0033, Japan

SOURCE: Angewandte Chemie, International Edition (2004),

43(25), 3258-3260

CODEN: ACIEF5; ISSN: 1433-7851

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 141:243143

AB The remarkably selective addition of ene carbamates R2CH:CR1NHCO2CH2Ph [R1 = Ph, 4-MeC6H4, 4-ClC6H4, 2-naphthyl, Et; R2 = H, Me, Et; R1R2 = (CH2)4] to

Et glyoxylate in the presence of a copper-dimine catalyst (0.1

mol%) gives the corresponding imines in high yields with

excellent enantioselectivities. A concerted aza-ene-type reaction

mechanism was proposed to explain the stereochem. outcome.

IT 697301-71-6 697301-72-7 697301-73-8 697301-74-9 697301-76-1 697301-77-2

750596-65-7

RL: RCT (Reactant); RACT (Reactant or reagent)

(stereoselective reactions of alkenylcarbamates with glyoxylate to give

syn and anti  $\alpha$ -alkyl- $\beta$ -hydroxy imines and ketones)

RN 697301-71-6 CAPLUS

CN Carbamic acid, N-(1-phenylethenyl)-, phenylmethyl ester (CA INDEX NAME)

RN 697301-72-7 CAPLUS

CN Carbamic acid, N-[1-(4-methoxyphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-73-8 CAPLUS

CN Carbamic acid, N-[1-(4-chlorophenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-74-9 CAPLUS

CN Carbamic acid, N-[1-(4-methylphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-76-1 CAPLUS

CN Carbamic acid, [(1E)-1-(4-methoxyphenyl)-1-propenyl]-, ethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 697301-77-2 CAPLUS

CN Carbamic acid, [(1Z)-1-(4-methoxyphenyl)-1-propenyl]-, ethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-65-7 CAPLUS

CN Carbamic acid, [1-(1-naphthalenyl)ethenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

IT 750596-67-9P 750596-68-0P 750596-69-1P

750596-70-4P 750596-71-5P 750596-72-6P

750596-73-7P 750596-74-8P 750596-75-9P

750596-76-0P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(stereoselective reactions of alkenylcarbamates with glyoxylate to give syn and anti  $\alpha$ -alkyl- $\beta$ -hydroxy imines and ketones)

RN 750596-67-9 CAPLUS

CN Carbamic acid, N-[(1E)-1-phenyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

$$\begin{array}{c|c} O & Ph \\ \hline Ph & & E \\ \hline Me \\ \end{array}$$

RN 750596-68-0 CAPLUS

CN Carbamic acid, N-[(1Z)-1-phenyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

RN 750596-69-1 CAPLUS

CN Carbamic acid, N-[(1E)-1-(4-methoxyphenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-70-4 CAPLUS

CN Carbamic acid, [(1Z)-1-(4-methoxyphenyl)-1-propenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-71-5 CAPLUS

CN Carbamic acid, N-[(1E)-1-(4-chlorophenyl)-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

RN 750596-72-6 CAPLUS

CN Carbamic acid, [(1Z)-1-(4-chlorophenyl)-1-propenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-73-7 CAPLUS

CN Carbamic acid, [(1E)-1-phenyl-1-butenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 750596-74-8 CAPLUS

CN Carbamic acid, [(1Z)-1-phenyl-1-butenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

RN 750596-75-9 CAPLUS

CN Carbamic acid, N-[(1E)-1-ethyl-1-propen-1-yl]-, phenylmethyl ester (CA INDEX NAME)

Double bond geometry as shown.

$$\begin{array}{c|c} & H & O & Ph \\ \hline Me & E & O & \end{array}$$

RN 750596-76-0 CAPLUS

CN Carbamic acid, [(1Z)-1-ethyl-1-propenyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

IT 750596-90-8P

RL: SPN (Synthetic preparation); PREP (Preparation) (stereoselective reactions of alkenylcarbamates with glyoxylate to give syn and anti  $\alpha$ -alkyl- $\beta$ -hydroxy imines and ketones)

RN 750596-90-8 CAPLUS

CN Carbamic acid, methyl(1-phenylethenyl)-, phenylmethyl ester (9CI) (CA INDEX NAME)

REFERENCE COUNT: 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 13 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2004:290653 CAPLUS

DOCUMENT NUMBER: 141:22992

TITLE: Copper(II)-catalyzed highly enantioselective

addition of enamides to imines: The use of enamides as nucleophiles in asymmetric catalysis

AUTHOR(S): Matsubara, Ryosuke; Nakamura, Yoshitaka; Kobayashi,

Shue

CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, The

University of Tokyo, Hongo, Bunkyo-ku, Tokyo,

113-0033, Japan

Page 42

SOURCE: Angewandte Chemie, International Edition (2004),

43(13), 1679-1681

CODEN: ACIEF5; ISSN: 1433-7851
PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 141:22992

GΙ

AB High-yielding efficient routes to optically active amino acid and 1,3-diamine derivs. have been achieved by the catalytic enantioselective addition of enamides to imines using a chiral copper catalyst. E.g., reaction of EtO2CCH:NCOC11H23 with MeCONHCPh:CH2 gave a  $\beta$ -amino imine, which was converted to a  $\beta$ -amino ketone I by treatment with acid. The catalysts used were Cu(OTf)2 in presence of chiral diamines. This reaction demonstrates the utility of enamides as nucleophiles. The reaction mechanism and the structure of the chiral

catalyst are also discussed.
IT 15728-00-4 52820-12-9 57957-24-1
697301-70-5 697301-71-6 697301-72-7
697301-73-8 697301-74-9 697301-75-0
697301-76-1 697301-77-2

RL: RCT (Reactant); RACT (Reactant or reagent)

(asym. preparation of amino acids and 1,3-diamine derivs. by copper (II)-catalyzed enantioselective addition of enamides to imines)

RN 15728-00-4 CAPLUS

CN Carbamic acid, (1-phenylethenyl)-, ethyl ester (9CI) (CA INDEX NAME)

RN 52820-12-9 CAPLUS

CN Carbamic acid, N-(1-methylethenyl)-, ethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} \text{O} & \text{CH}_2 \\ \parallel & \parallel \\ \text{EtO-C-NH-C-Me} \end{array}$$

RN 57957-24-1 CAPLUS

CN Acetamide, N-(1-phenylethenyl)- (CA INDEX NAME)

RN 697301-70-5 CAPLUS

CN Carbamic acid, N-(1-phenylethenyl)-, 1,1-dimethylethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} CH_2 & O \\ \parallel & \parallel \\ Ph-C-NH-C-OBu-t \end{array}$$

RN 697301-71-6 CAPLUS

CN Carbamic acid, N-(1-phenylethenyl)-, phenylmethyl ester (CA INDEX NAME)

RN 697301-72-7 CAPLUS

CN Carbamic acid, N-[1-(4-methoxyphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-73-8 CAPLUS

CN Carbamic acid, N-[1-(4-chlorophenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-74-9 CAPLUS

CN Carbamic acid, N-[1-(4-methylphenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

$$\begin{array}{c|c} \text{CH}_2 & \text{O} \\ \parallel & \parallel \\ \text{C-NH-C-O-CH}_2\text{-Ph} \\ \\ \text{Me} \end{array}$$

RN 697301-75-0 CAPLUS

CN Carbamic acid, N-[1-(2-naphthalenyl)ethenyl]-, phenylmethyl ester (CA INDEX NAME)

RN 697301-76-1 CAPLUS

CN Carbamic acid, [(1E)-1-(4-methoxyphenyl)-1-propenyl]-, ethyl ester (9CI) (CA INDEX NAME)

Double bond geometry as shown.

RN 697301-77-2 CAPLUS

CN Carbamic acid, [(1Z)-1-(4-methoxyphenyl)-1-propenyl]-, ethyl ester (9CI) (CA INDEX NAME)

IT 72012-52-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(asym. preparation of amino acids and 1,3-diamine derivs. by copper (II)-catalyzed enantioselective addition of enamides to imines)

RN 72012-52-3 CAPLUS

CN Acetamide, N-methyl-N-(1-phenylethenyl)- (CA INDEX NAME)

 $\begin{array}{c|c} \text{H}_2\text{C} & \text{Me} \\ & || & | \\ \text{Ph-C-N-Ac} \end{array}$ 

REFERENCE COUNT: 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 14 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2004:177965 CAPLUS

DOCUMENT NUMBER: 140:235900

TITLE: Preparation of chiral diphosphines and their

transition metal complexes and their use in asymmetric

synthesis

INVENTOR(S): Meseguer, Benjamin; Militzer, Hans-Christian;

Castillon, Sergio; Claver, Carmen; Diaz, Yolanda; Aghmiz, Mohamed; Guiu, Esther; Aghmiz, Ali; Masdeu,

Anna

PATENT ASSIGNEE(S): Bayer A.-G., Germany SOURCE: Ger. Offen., 34 pp.

CODEN: GWXXBX

DOCUMENT TYPE: Patent LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE		
DE 10241256 EP 1400527 EP 1400527	A1 A1 B1	20040304 20040324 20060322	DE 2002-10241256 EP 2003-18221	20020906 20030811		
R: AT, BE, CH,	DE, DK	, ES, FR, GB	, GR, IT, LI, LU, NL, , AL, TR, BG, CZ, EE,			
AT 321059 ES 2259400	T T3	20060415 20061001	AT 2003-18221 ES 2003-18221	20030811 20030811		
IN 2003DN00996 US 20050080047	A A1	20050527 20050414	IN 2003-DN996 US 2003-643552	20030814 20030819		
US 7193092 JP 2004161741	B2 A	20070320 20040610	JP 2003-208112	20030820		
CN 1493576 US 20070155971	A A1	20040505 20070705	CN 2003-158087 US 2007-707710	20030821 20070216		
PRIORITY APPLN. INFO.:			DE 2002-10238115 DE 2002-10241256	IA 20020821 A 20020906		
OTHER SOURCE (S).	CASDEA	CT 1/0.23590	US 2003-643552	A3 20030819		

OTHER SOURCE(S): CASREACT 140:235900; MARPAT 140:235900

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The present invention concerns the preparation of chiral diphosphines their transition metal complexes, and use of complexes in asym. syntheses.

Thus, preparation of 2,3-bis-O-(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-D-mannitol I, prepared from 1,6-dideoxy-2,5-anhydro-D-mannitol, and [Rh(cod)2]BF4/I catalyzed enantioselective hydrogenation of CH2:C(NHAc)(CO2Me) is described.

IT 35356-70-8 52386-78-4 57957-24-1

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of chiral diphosphines and its transition metal complexes and their use in asym. synthesis)

RN 35356-70-8 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-, methyl ester (CA INDEX NAME)

$$\begin{array}{c|c} \text{H}_2\text{C} & \text{O} \\ & || & || \\ \text{AcNH-C-C-OMe} \end{array}$$

RN 52386-78-4 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-phenyl-, methyl ester (CA INDEX NAME)

$$Ph-CH = \begin{array}{c} NHAc \\ | \\ C-C-OMe \\ | \\ | \\ O \end{array}$$

RN 57957-24-1 CAPLUS

CN Acetamide, N-(1-phenylethenyl) - (CA INDEX NAME)

$$\begin{array}{c} \text{CH}_2 \\ || \\ \text{Ph-C-NHAc} \end{array}$$

L18 ANSWER 15 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2002:835619 CAPLUS

DOCUMENT NUMBER: 138:401626

TITLE: Product class 12: oxazoles

### Page 47

AUTHOR(S): Boyd, G. V.

CORPORATE SOURCE: Givataim, 53460, Israel

SOURCE: Science of Synthesis (2002), 11, 383-479

CODEN: SSCYJ9

PUBLISHER: Georg Thieme Verlag
DOCUMENT TYPE: Journal; General Review

LANGUAGE: English

AB A review of the synthesis of simple and condensed oxazoles. Reaction covered include addition, cycloaddn., heterocyclization, hydrolysis.

IT 99990-33-7 101735-38-0 106274-54-8

526212-81-7

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of oxazoles via cyclization of N-acyl- $\beta$ -halo enamines)

RN 99990-33-7 CAPLUS

CN 2-Butenoic acid, 2-(benzoylamino)-3-bromo-, methyl ester (CA INDEX NAME)

RN 101735-38-0 CAPLUS

CN 2-Propenoic acid, 2-(benzoylamino)-3-bromo-3-phenyl-, ethyl ester (CA INDEX NAME)

RN 106274-54-8 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-bromo-3-phenyl-, ethyl ester (CA INDEX NAME)

RN 526212-81-7 CAPLUS

CN Acetamide, N-[2-bromo-1-cyano-2-(methylamino)ethenyl]- (CA INDEX NAME)

AcNH Br NC-C=C-NHMe

REFERENCE COUNT:

238 THERE ARE 238 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 16 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

2002:832759 CAPLUS ACCESSION NUMBER:

DOCUMENT NUMBER: 137:353062

TITLE: Preparation of 2-iminopyrrolidine

derivatives as thrombin receptor antagonists

INVENTOR(S): Suzuki, Shuichi; Kotake, Makoto; Miyamoto, Mitsuaki;

Kawahara, Tetsuya; Kajiwara, Akiharu; Hishinuma, Ieharu; Okano, Kazuo; Miyazawa, Syuhei; Clark, Richard; Ozaki, Fumihiro; Sato, Nobuaki; Shinoda, Masanobu; Kamada, Atsushi; Tsukada, Itaru; Matsuura, Fumiyoshi; Naoe, Yoshimitsu; Terauchi, Taro; Oohashi, Yoshiaki; Ito, Osamu; Tanaka, Hiroshi; Musya, Takashi; Kogushi, Motoji; Kawada, Tsutomu; Matsuoka, Toshiyuki; Kobayashi, Hiroko; Chiba, Kenichi; Kimura, Akifumi;

Ono, Naoto

PATENT ASSIGNEE(S): Eisai Co., Ltd., Japan SOURCE:

PCT Int. Appl., 948 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 4

PATENT INFORMATION:

PATENT NO. KIND DATE APPLICATION NO.										D.	ATE						
WO	2002	0858	 55		A1	_	2002	1031		WO 2	002-	 JР39	 61		2	0020	419
	W:	ΑE,	AG,	AL,	AM,	ΑT,	ΑU,	ΑZ,	BA,	BB,	BG,	BR,	BY,	BZ,	CA,	CH,	CN,
		CO,	CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EC,	EE,	ES,	FI,	GB,	GD,	GE,	GH,
		GM,	HR,	HU,	ID,	IL,	IN,	IS,	JP,	KΕ,	KG,	KP,	KR,	KΖ,	LC,	LK,	LR,
		LS,	LT,	LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NO,	NΖ,	OM,	PH,
		PL,	PT,	RO,	RU,	SD,	SE,	SG,	SI,	SK,	SL,	ΤJ,	TM,	TN,	TR,	TT,	TZ,
		UA,	UG,	US,	UZ,	VN,	YU,	ZA,	ZM,	ZW							
	RW:	GH,	GM,	KE,	LS,	MW,	MZ,	SD,	SL,	SZ,	TZ,	UG,	ZM,	ZW,	AT,	BE,	CH,
				•	•		FR,	•		•		•	•	•	•	•	•
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	2446						2002										
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		2552															
EP	1391	-					2004					-	-				-
	R:	AT,										LI,	LU,	NL,	SE,	MC,	PT,
							RO,										
		0089					2004										
	1503						2004		1	CN 2	002-	8085	65		2	0020	419
	1243						2006										
		0004	-				2005										
	1614						2006	-		EP 2	005-	2206	9		2	0020	419
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CN	1733	,	,	/	A		2006	0215		CN	200!	5-1	008	0404			200	20	419
CN	10040	0249	9		С		2008												
	2270				C2		2006			RU	2003	3-1	336	64			200	20	419
CN	17548	880			A		2006	0405		CN	200	5-1	.008	0403			200	20	419
CN	13219	996			С		2007	0620											
JP	3795	458			В2		2006	0712		JΡ	2002	2-5	833	82			200	20	419
NZ	52882	20			Α		2007	0126		NZ	2002	2-5	288	20			200	20	419
AT	42596	64			T		2009	0415		ΑT	2002	2-7	7205	34					419
MX	20030	0094	97		A		2004	0524			2003						200	31	016
	2003		64		А		2005				2003								016
	74979				В1		2007				2003								018
	20031		-		Α		2005				2003								020
	20050		204		A1		2005			US	200	4-4	1751	88			200	40	609
	7244				В2		2007												
	20052				A1		2005			AU	200!	5-2	2021	35			200	)50.	517
	2005		35		В2		2007												
	74979				В1		2007				200!								526
	20050				A1		2005				200!	-							622
	20062				A		2006				2000								217
	20062		93		A		2006				2000								217
	10862		0.00		A1		2008				2000								601
	20061				Α		2008	OROI			2000					70			107
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AB 2-Iminopyrrolidine derivs. including 2,3-dihydro-1H-isoindole and 6,7-dihydro-5H-pyrrolo[3,4-b]pyridine represented by the general formula (I) or salts thereof [wherein B = (un)substituted aromatic hydrocarbon or aromatic heterocyclic ring optionally containing 1 or 2 N atom(s);

R101, R102, R103 = H, cyano, halo, each (un)substituted C1-6 alkyl, C2-8 alkenyl, C2-8 alkynyl, acyl, CO2H, CONH2, C1-6 alkoxycarbonyl, C1-6 alkylaminocarbonyl, HO, C1-6 alkoxy, C3-8 cycloalkyloxy, NH2, C1-6 alkylamino, C3-8 cycloalkylamino, acylamino, ureido, sulfonylamino, sulfonyl, SO2NH2, or C3-8 cycloalkyl, etc.; Y1 = a single bond, (CH2)m, each (un) substituted CH, CH2, NH, CONH, or SO2NH, CH2CO, SO, SO2, CO (wherein m = an integer of 1-3); Y2 = a single bond, O, N, (CH2)m, each (un) substituted CH, CH2, or C(:NOH), CO, SO, SO2; Ar = H, (un) substituted Ph] are prepared These compds. are thrombin receptor antagonists, in particular thrombin PAR1 receptor antagonists and are useful as blood platelet aggregation inhibitors and proliferation inhibitors of smooth muscle cell, endothelial cell, fibroblast, kidney cell, osteosarcoma cell, muscle cell, cancer cell, and/or glial cell and for the treatment and/or prevention of thrombosis, vascular restenosis, deep vein thrombosis, lung embolism, cerebral infarction, heart disease, disseminated intravascular coagulation syndrome, hypertension, inflammation, rheumatism, asthma, glomerulonephritis, osteoporosis, nerve disease, and/or malignant tumor. Thus, [6-[(1-imino-1,3-dihydroisoindol-2-yl)acetyl]-2,3dihydrobenz[1,4]oxazin-4-yl]acetonitrile derivative (II) in vitro showed IC50 of 0.017  $\mu\text{M}$  for inhibiting the binding of [3H]Ala-(4-fluoro)Phe-Arg-(cyclohexyl)Ala-homoArg-Tyr-NH2 to thrombin receptor of human blood platelet, that of 0.29  $\mu M$  for inhibiting the human blood platelet aggregation induced by thrombin, and that of 0.0061  $\mu\text{M}$  for inhibiting the proliferation of rat smooth cell. 474546-41-3P 474546-55-9P 474546-70-8P

RL: PAC (Pharmacological activity); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)

(preparation of dihydroisoindole and dihydro-5H-pyrrolo[3,4-b]pyridine

### Page 51

derivs. as thrombin receptor antagonists and remedies and/or preventives for diseases)

RN 474546-41-3 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-[2-(1,1-dimethylethyl)-4-[2-(2-ethyl-5,7-dihydro-7-imino-6H-pyrrolo[3,4-b]pyridin-6-yl)acetyl]phenyl]-, methyl ester, hydrobromide (1:1) (CA INDEX NAME)

## • HBr

RN 474546-55-9 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-[4-[2-(5,6-diethoxy-7-fluoro-1,3-dihydro-1-imino-2H-isoindol-2-yl)acetyl]-2-(1,1-dimethylethyl)phenyl]-, methyl ester, hydrobromide (1:1) (CA INDEX NAME)

## • HBr

RN 474546-70-8 CAPLUS

CN 2-Propenoic acid, 2-(acetylamino)-3-[2-(1,1-dimethylethyl)-4-[2-[5-ethoxy-1,3-dihydro-1-imino-6-[(methylamino)carbonyl]-2H-isoindol-2-yl]acetyl]phenyl]-, methyl ester, hydrobromide (1:1) (CA INDEX NAME)

$$\begin{array}{c|c} & & & & \\ & &$$

HBr

REFERENCE COUNT: 100 THERE ARE 100 CITED REFERENCES AVAILABLE FOR

THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE

FORMAT

L18 ANSWER 17 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2002:832746 CAPLUS

DOCUMENT NUMBER: 137:352492

TITLE: Copper-catalyzed formation of

carbon-heteroatom and carbon-carbon bonds by arylation

and vinylation of amines, amides, hydrazides,

heterocycles, alcohols, enolates, and malonates, using

aryl, heteroaryl, and vinyl halides and analogs

INVENTOR(S): Buchwald, Stephen L.; Klapars, Artis; Antilla, Jon C.;

Job, Gabriel E.; Wolter, Martina; Kwong, Fuk Y.;

Nordmann, Gero; Hennessy, Edward J.

PATENT ASSIGNEE(S): Massachusetts Institute of Technology, USA

SOURCE: PCT Int. Appl., 306 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.					KIN	D	DATE			APPL	ICAT	ION :	NO.		D	ATE	
WO 2002085838					A1 20021031			WO 2002-US12785						20020424			
	W:	ΑE,	AG,	AL,	AM,	ΑT,	ΑU,	AZ,	BA,	BB,	BG,	BR,	BY,	BZ,	CA,	CH,	CN,
		CO,	CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EC,	EE,	ES,	FΙ,	GB,	GD,	GE,	GH,
		GM,	HR,	HU,	ID,	IL,	IN,	IS,	JP,	KE,	KG,	KP,	KR,	KΖ,	LC,	LK,	LR,
		LS,	LT,	LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NO,	NZ,	OM,	PH,
		PL,	PT,	RO,	RU,	SD,	SE,	SG,	SI,	SK,	SL,	ΤJ,	TM,	TN,	TR,	TT,	TZ,
		UA,	UG,	UZ,	VN,	YU,	ZA,	ZM,	ZW								
	RW:	GH,	GM,	KE,	LS,	MW,	MZ,	SD,	SL,	SZ,	TZ,	UG,	ZM,	ZW,	AT,	BE,	CH,
							FR,										
		BF,	ВJ,	CF,	CG,	CI,	CM,	GA,	GN,	GQ,	GW,	ML,	MR,	NE,	SN,	TD,	TG
CA	2445	159			A1		2002	1031		CA 2002-2445159					2	0020	424
ΑU	2002	2589	46		A1		2002	1105		AU 2	002-	2589	46		2	0020	424
US	2003	0065	187		A1		2003	0403		US 2	002-	1289	81		2	0020	424
US	6759	554			В2		2004	0706									
ΕP	1390	340			A1		2004	0225		EP 2	002-	7289	25		2	0020	424

	R:	ΑT,	BE,	CH,	DE,	DK,	ES,	FR,	GB,	GF	R, IT	, LI,	LU,	NL,	SE	, MC,	PT,
		ΙE,	SI,	LT,	LV,	FI,	RO,	MK,	CY,	ΑI	J, TR						
CN	1518	534			A		2004	0804	1	CN	2002	-8125	87			20020	424
CN	1266	112			С		2006	0726									
JP	2004	5367	98		${ m T}$		2004	1209		JΡ	2002	-5833	66			20020	424
CN	1854	128			A		2006	1101	1	CN	2006	-1008	2481			20020	424
US	2004	0019	216		A1		2004	0129		US	2003	-4357	19			20030	508
US	6867	298			В2		2005	0315									
US	2005	0215	794		A1		2005	0929		US	2005	-2850	0			20050	104
US	7115	784			В2		2006	1003									
US	2006	0264	673		A1		2006	1123		US	2006	-4311	54			20060	509
PRIORIT	Y APP	LN.	INFO	.:						US	2001	-2862	68P		Р	20010	424
										US	2001	-3480	14P		Р	20011	024
										US	2001	-3442	08P		Р	20011	221
									1	CN	2002	-8125	87		ΑЗ	20020	424
										US	2002	-1289	81		A3	20020	424
									,	WO	2002	-US12	785		W	20020	424
										US	2003	-4357	19		ΑЗ	20030	508
										US	2005	-2850	0		ΑЗ	20050	104
OTHER SO	DURCE	(S):			CASI	REAC	T 13	7:352	2492	• N	(ARPA	т 137	.352	492			

OTHER SOURCE(S): CASREACT 137:352492; MARPAT 137:352492

AB The invention relates to copper-catalyzed carbon-heteroatom and carbon-carbon bond-forming methods. More specifically, it relates to the arylation, heteroarylation, and vinylation of compds. with nucleophilic N, O, and C atoms, by aryl and vinyl halides and sulfonates, using various Cu-based catalysts and suitable ligands. The methods provide an inexpensive alternative to corresponding palladium-catalyzed reactions. Thus, the invention includes copper-catalyzed methods of forming a carbon-nitrogen bond between the nitrogen atom of an amide or amine moiety and the activated carbon of an aryl, heteroaryl, or vinyl halide or sulfonate. The invention provides similar copper-catalyzed reactions of acyl hydrazines (i.e., hydrazides). The invention further relates to copper-catalyzed arylation and vinylation of nitrogen-containing heteroaroms., e.g., indole, pyrazole, and indazole, at nitrogen. Similarly, the invention provides copper-catalyzed

arylation and vinylation of alcs. at the oxygen atom. Finally, the invention provides copper-catalyzed methods of forming a carbon-carbon bond between reactants with nucleophilic carbon atoms, e.g., an enolate or malonate anion, and the activated carbon of the aryl, heteroaryl, or vinyl halides or sulfonates. Importantly, all of the invention methods are relatively inexpensive to practice due to the low cost of the copper catalysts. For example, a claimed method for amines, amides, and hydrazides involves reaction of halides and sulfonates Z-X [Z = (un)substituted aryl, heteroaryl, or alkenyl; X = iodo, Br, Cl, alkylsulfonate, arylsulfonate] with amines and derivs. R-NH-R' [R = alkyl, cycloalkyl aralkyl, aryl, heteroaryl, formyl, acyl, alkoxycarbonyl, aryloxycarbonyl, acylamino, etc.; R' = H, alkyl, cycloalkyl, (hetero)aralkyl, (hetero)aryl, formyl, acyl, amino, or amidino; with provisos] in the presence of a copper atom or ion and a ligand in the presence of a Bronsted base, yielding a corresponding arylated or vinylated product Z-NRR'. Thus, arylation of benzamide with allyl 4-iodobenzoate in dioxane solvent in the presence of CuI (catalyst), trans-1,2-cyclohexanediamine (ligand), and K3PO4 (base), at 110° in a resealable Schlenk tube, gave the expected product I in 91% yield. Similarly, 2-pyrrolidinone was N-heteroarylated by 2-iodothiophene under the same conditions to give II in quant. yield. Indole was N-arylated by 4-bromotoluene to give III in 95% yield. A similar reaction of (E)-2-undecen-1-ol with (E)-1-iodo-1-decene using CuI, 3,4,7,8-tetramethyl-1,10-phenanthroline, and Cs2CO3 in PhMe at 80°, gave 68% (E,E)-1-(dec-1-enyloxy)undec-2-ene. 474352-83-5P, trans-N-(1-Hexenyl)benzamide RL: SPN (Synthetic preparation); PREP (Preparation)

ΙT

(alkenylation product; inexpensive copper-catalyzed arylation and vinylation of amines, amides, heterocycles, alcs., and enolates, using aryl, heteroaryl, and vinyl halides and analogs)

474352-83-5 CAPLUS RN

Benzamide, N-(1E)-1-hexen-1-yl- (CA INDEX NAME) CN

Double bond geometry as shown.

REFERENCE COUNT: THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS 1 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 18 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

2002:152980 CAPLUS ACCESSION NUMBER:

DOCUMENT NUMBER: 136:202281

TITLE: Absorption refrigerator with hydrophilic coatings on

heat exchanger tubes.

Ozaki, Toshinori; Kodaira, Muneo; Nakai, Takeshi; INVENTOR(S):

Horiguchi, Masaru; Miyaji, Takashi; Kiyofuji, Masahiro

PATENT ASSIGNEE(S): Hitachi Cable, Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO. KIND DATE APPLICATION NO. DATE

JP 2002061987 A 20020228 JP 2000-250447 20000822

PRIORITY APPLN. INFO:: JP 2000-250447 20000822

AB The title apparatus is characterized by including heat exchanger tubes (e.g., Cu tubes) having surfaces coated with colloidal silica, water glass, silica hydrate, glassy silica or tridymite mixture to form hydrophilic coating films, resp., and refrigerant accommodating sections having liquid-phase or gas-phase refrigerants contacting with the heat exchanger tubes; the refrigerants contain saturated dissolved silica component or hydrophilic agent. The refrigerant accommodating sections include regenerator and absorber accommodated with LiBr-containing refrigerant containing

silica component concentration 10,000-28,000 ppm, evaporator and condenser accommodated with pure water refrigerant containing silica component concentration

500-840 ppm, and circulating pipelines.

IT 28408-65-3, Acetamide, N-ethenyl-, homopolymer

RL: TEM (Technical or engineered material use); USES (Uses) (hydrophilic coatings containing; absorption refrigerator with hydrophilic coatings on heat exchanger tubes)

RN 28408-65-3 CAPLUS

CN Acetamide, N-ethenyl-, homopolymer (CA INDEX NAME)

CM 1

CRN 5202-78-8 CMF C4 H7 N O

AcNH-CH-CH2

L18 ANSWER 19 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2001:321284 CAPLUS

DOCUMENT NUMBER: 135:122004

TITLE: Cross-coupling of non-stabilized aziridinylmagnesiums

with alkyl halides catalyzed by Cu(I) iodide: a new synthesis of amines bearing a quaternary chiral center and an asymmetric synthesis of both enantiomers of the

amines from one chiral starting material

AUTHOR(S): Satoh, T.; Matsue, R.; Fujii, T.; Morikawa, S.

CORPORATE SOURCE: Faculty of Science, Department of Chemistry, Science

University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo,

162-8601, Japan

SOURCE: Tetrahedron (2001), 57(18), 3891-3898

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Science Ltd.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 135:122004

AB Treatment of sulfinylaziridines, which were synthesized from 1-chloroalkyl p-tolyl sulfoxides and imines, with ethylmagnesium bromide gave

non-stabilized aziridinylmagnesiums by a sulfoxide-magnesium exchange reaction. The cross-coupling of the aziridinylmagnesiums with various kinds of alkyl halides was realized in high yields by using Cu(I) iodide as a catalyst, and the reaction was found to be stereospecific. The coupling products were hydrogenated with Pd(OH)2 in alc. to give the amines bearing a quaternary chiral center in quant. yields. Synthesis of both enantiomers of the amines bearing a quaternary chiral center was realized starting from optically active (R)-chloromethyl p-tolyl sulfoxide in good overall yields with perfect asym. induction. For example, treatment of  $(-)-(2R,3R)-2-\text{decyl}-2-[(R)-(4-\text{methylphenyl})\,\text{sulfinyl}]-1,3$ diphenylaziridine with ethylmagnesium bromide in dry THF gave the corresponding (aziridinyl) magnesium in situ. Addition of iodomethane and copper iodide (CuI) to the solution containing the (aziridinyl)magnesium gave (-)-(2S,3R)-2-decyl-2-methyl-1,3-diphenylaziridine. Hydrogenolysis of the latter gave (+)-( $\alpha$ S)- $\alpha$ -decyl- $\alpha$ -methyl-Nphenylbenzeneethanamine.

IT 351388-17-5P

RN

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of chiral amines by cross-coupling of (aziridinyl)magnesium with alkyl halides catalyzed by copper iodide) 351388-17-5 CAPLUS

REFERENCE COUNT: 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 20 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2001:152619 CAPLUS

DOCUMENT NUMBER: 134:207966

TITLE: Chiral ligands, transition-metal complexes thereof and

uses thereof in asymmetric reactions

INVENTOR(S): Zhang, Xumu; Xiao, Dengming

PATENT ASSIGNEE(S): The Penn State Research Foundation, USA

SOURCE: PCT Int. Appl., 69 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND DATE	APPLICATION NO.	DATE
WO 2001014299	A1 2001030	1 WO 2000-US22976	20000822
W: AE, AL, AM,	AT, AU, AZ, BA	, BB, BG, BR, BY, CA, CH	, CN, CR, CU,
CZ, DE, DK,	DM, EE, ES, FI	, GB, GD, GE, GH, GM, HR	, HU, ID, IL,
IN, IS, JP,	KE, KG, KP, KR	, KZ, LC, LK, LR, LS, LT	, LU, LV, MA,
MD, MG, MK,	MN, MW, MX, NC	, NZ, PL, PT, RO, RU, SD	, SE, SG, SI,
SK, SL, TJ,	TM, TR, TT, TZ	, UA, UG, UZ, VN, YU, ZA	, ZW

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RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY,
             DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ,
             CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG
     CA 2382779
                                20010301
                                            CA 2000-2382779
                                                                     20000822
                          Α1
                                             EP 2000-961346
     EP 1206427
                          A1
                                20020522
                                                                    20000822
     EP 1206427
                                 20051109
                          В1
            AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
             IE, SI, LT, LV, FI, RO, MK, CY, AL
     JP 2003507443
                          Τ
                                20030225
                                             JP 2001-518392
                                                                     20000822
     US 6525210
                          В1
                                20030225
                                             US 2000-643434
                                                                    20000822
                                             AT 2000-961346
     AT 309186
                          Τ
                                20051115
                                                                    20000822
     ES 2254218
                          Т3
                                20060616
                                             ES 2000-961346
                                                                    20000822
     US 20030163003
                                20030828
                                             US 2002-319093
                                                                    20021213
                          Α1
     US 6828271
                                20041207
                          В2
PRIORITY APPLN. INFO.:
                                             US 1999-150375P
                                                                    19990823
                                                                 Р
                                                                 P 19991115
                                             US 1999-165649P
                                             US 2000-643434
                                                                 A3 20000822
                                             WO 2000-US22976
                                                                 W 20000822
                        CASREACT 134:207966; MARPAT 134:207966
OTHER SOURCE(S):
GΙ
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Ι

Chiral ligands and transition metal complexes based on such chiral ligands useful in asym. catalysis are disclosed. The chiral ligands include phospholanes, P,N ligands, N,N ligands, biphenols, and chelating phosphines, e.g. I. The ferrocene-based iridium (R,R)-f-binaphane complex reduces imines to the corresponding amines with 95-99.6 % enantioselectivity and reduces  $\beta$ -substituted- $\alpha$ -arylenamides with 95 % enantioselectivity. The transition metal complexes of the chiral ligands are useful in asym. reactions such as asym. hydrogenation of imines, asym. hydride transfer reactions, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, allylic alkylation, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition and epoxidn. reactions.

60544-12-9 177750-09-3 177750-16-2
177750-24-2 218903-49-2 218903-53-8
222415-38-5 222984-41-0 251545-86-5
251545-89-8
RL: RCT (Reactant); RACT (Reactant or reagent)
(binaphane rhodium complex catalyzed enantioselective hydrogenation of)
RN 2700-50-7 CAPLUS
CN Acetamide, N-[1-(4-methoxyphenyl)-1-propen-1-yl]- (CA INDEX NAME)

RN 2890-85-9 CAPLUS CN Acetamide, N-(1-phenyl-1-propen-1-yl)- (CA INDEX NAME)

RN 57957-24-1 CAPLUS CN Acetamide, N-(1-phenylethenyl)- (CA INDEX NAME)

$$\begin{array}{c} \text{CH}_2 \\ || \\ \text{Ph-C-NHAc} \end{array}$$

RN 60544-12-9 CAPLUS CN Acetamide, N-(1-phenyl-1-buten-1-yl)- (CA INDEX NAME)

$$\begin{array}{c} \text{Ph} \\ | \\ \text{AcNH-C----} \text{CH-Et} \end{array}$$

RN 177750-09-3 CAPLUS
CN Acetamide, N-[1-[4-(trifluoromethyl)phenyl]ethenyl]- (CA INDEX NAME)

# Page 59

RN 177750-16-2 CAPLUS

CN Acetamide, N-[1-(3-methylphenyl)ethenyl]- (CA INDEX NAME)

RN 177750-24-2 CAPLUS

CN Acetamide, N-[1-(2-naphthalenyl)ethenyl]- (CA INDEX NAME)

RN 218903-49-2 CAPLUS

CN Acetamide, N-(1-[1,1'-biphenyl]-4-ylethenyl)- (CA INDEX NAME)

Ph

RN 218903-53-8 CAPLUS

CN Acetamide, N-[1-(2-naphthalenyl)-1-propen-1-yl]- (CA INDEX NAME)

RN 222415-38-5 CAPLUS

CN Acetamide, N-[1-[4-(trifluoromethyl)phenyl]-1-propen-1-yl]- (CA INDEX NAME)

RN 222984-41-0 CAPLUS

CN Acetamide, N-(3-methyl-1-phenyl-1-buten-1-yl)- (CA INDEX NAME)

RN 251545-86-5 CAPLUS

CN Acetamide, N-(1,3-diphenyl-1-propen-1-yl)- (CA INDEX NAME)

$$\Pr_{\mid}$$
 Acnh-C=CH-CH<sub>2</sub>-Ph

RN 251545-89-8 CAPLUS

CN Acetamide, N-[1-(4-cyclohexylphenyl)ethenyl]- (CA INDEX NAME)

REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 21 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2000:805739 CAPLUS

DOCUMENT NUMBER: 134:56752

TITLE: Stabilized bismuthonium ylides bearing a highly cross-conjugated ylidic carbon atom: synthesis,

structures, and reactions

AUTHOR(S): Matano, Yoshihiro; Nomura, Hazumi; Suzuki, Hitomi CORPORATE SOURCE: Department of Chemistry, Graduate School of Science

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan

SOURCE: Journal of Organometallic Chemistry (2000), 611(1-2),

89-99

CODEN: JORCAI; ISSN: 0022-328X

PUBLISHER: Elsevier Science S.A.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 134:56752

The reaction of iminotriaryl- $\lambda 5$ -bismuthanes Ar3Bi:NR (2; AΒ Ar = o-MeC6H4, o-MeOC6H4 R = COCF3, COC6H3(CF3)2-3,5, COC6H4NO2-4; Ar = o-MeC6H4o-MeOC6H4, R = COC6H4CN-4; Ar = p-MeC6H4, R = SO2CF3, SO2Ph; Ar = Ph, R = PhSO2C6H4Me-p) with dialkyl acetylenedicarboxylates R'O2CC.tplbond.CCO2R' (3; R' = Me, Et) was found to afford highly stabilized bismuthonium ylides Ar3Bi:C(CO2R')C(CO2R'):NR (4; Ar, R, R' = same as above) in 50-92% yield. The x-ray crystallog, analyses of two of these ylides (o-MeC6H4)3Bi:C(CO2Me)C(CO2Me):NR (R = COCF3, COC6H4NO2-4) demonstrated that their Bi center possesses a distorted tetrahedral geometry with the highly cross-conjugated ylidic C atom. The observed Bi-Cylide bond lengths of 2.178(7)-2.199(7) Å are close to ordinary Bi-CAr bond lengths, suggesting an appreciable single bond character of the Bi-Cylide bond. The action of two equivalent of HOAc, HCl, or 4-nitrophenol on several 4 cleaved the Bi-Cylide bond to give the corresponding triarylbismuth(V) compds. Ar3BiX2 (Ar = o-MeOC6H4, X = OAc; Ar = p-MeC6H4, X = C1, OC6H4NO2-4) and olefins MeO2CCH=C(CO2Me)NHR (5; R = COC6H3(CF3)2-3,5, SO2Ph). 4-Nitrobenzenethiol was oxidized by 0.5 equiv of 4 (Ar = p-MeC6H4, R = SO2Ph, R' = Me) to give bis(4-nitrophenyl) disulfide with a good recovery of triarylbismuthine (p-MeC6H4)3Bi and olefin MeO2CC:C(CO2Me)NHSO2Ph. On thermolysis at 200°, or when decomposed in the presence of a Cu catalyst at room temperature, the ylides Ar3Bi:C(CO2MeR)C(CO2Me):NR (Ar = o-MeC6H4, R = COC6H4-4-NO2; Ar = COC6H4-4-NO2) o-MeOC6H4, R = COC6H3(CF3)2-3,5, COC6H4CN-4) bearing an N-aroyl group gave 2,4,5-trisubstituted oxazoles 7 (shown as I, Ar as defined above) and triarylbismuthines 6 Ar3Bi (Ar = o-MeC6H4, o-MeOC6H4) in moderate to excellent yields.

RN 313974-17-3 CAPLUS

CN 2-Butenedioic acid, 2-[[3,5-bis(trifluoromethyl)benzoyl]amino]-, 1,4-dimethyl ester, (2Z)- (CA INDEX NAME)

RN 313974-19-5 CAPLUS

CN 2-Butenedioic acid, 2-[[3,5-bis(trifluoromethyl)benzoyl]amino]-, 1,4-dimethyl ester, (2E)- (CA INDEX NAME)

Double bond geometry as shown.

REFERENCE COUNT: 43 THERE ARE 43 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L18 ANSWER 22 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 1992:470465 CAPLUS

DOCUMENT NUMBER: 117:70465

ORIGINAL REFERENCE NO.: 117:12419a,12422a

TITLE: Functionalization and chelating properties of a porous

polymer derived from vinylamine

AUTHOR(S): Tbal, Hamid; Delporte, Michele; Morcellet, Joelle;

Morcellet, Michel

CORPORATE SOURCE: Lab. Chim. Macromol., Univ. Sci. Tech. Lille,

Villeneuve d'Ascq, 59655, Fr.

SOURCE: European Polymer Journal (1992), 28(6), 671-9

CODEN: EUPJAG; ISSN: 0014-3057

DOCUMENT TYPE: Journal LANGUAGE: English

AB A porous polymer containing vinylamine units was prepared by suspension copolymn. of N-vinyl tert-Bu carbamate, styrene, and ethylene glycol dimethacrylate in the presence of heptane, followed by hydrolysis of the carbamate functions to obtain amino groups. This crosslinked polymer had sp. surface area 16 m2/g, porous volume 1.32 cm3/g, and contained 3.75 meq/g amino functions. It was then subjected to a series of chemical reactions in order to introduce specific chelating ligands, viz. iminodiacetic , aminophosphonic, thiourea, and dithiocarbamate. The chelating properties of these functionalized polymers toward Cu and U were then

determined by the batch method. Most of them possessed high capacities compared to com. resins crosslinked with divinylbenzene.

IT 28497-66-7DP, hydrolyzed, functional derivs. 121876-39-9DP, hydrolyzed, functional derivs.

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation and complexation of, with copper and uranium)

RN 28497-66-7 CAPLUS

CN Carbamic acid, ethenyl-, 1,1-dimethylethyl ester, homopolymer (9CI) (CA INDEX NAME)

CM 1

CRN 7150-72-3 CMF C7 H13 N O2

RN 121876-39-9 CAPLUS

CN 2-Propenoic acid, 2-methyl-, 1,2-ethanediyl ester, polymer with 1,1-dimethylethyl ethenylcarbamate and ethenylbenzene (9CI) (CA INDEX NAME)

CM 1

CRN 7150-72-3 CMF C7 H13 N O2

CM 2

CRN 100-42-5 CMF C8 H8

 $H_2C = CH - Ph$ 

CM 3

CRN 97-90-5 CMF C10 H14 O4

L18 ANSWER 23 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 1991:93978 CAPLUS

DOCUMENT NUMBER: 114:93978

ORIGINAL REFERENCE NO.: 114:15813a,15816a

TITLE: Complexing ability of a new type of bis-amidato

ligand. Crystal structure of

N, N'-bis(1-methyl-3-oxo-1-butenyl)oxamidatocopper(II) (CuL); spectroscopic and magnetic properties and redox behavior of CuL and the related nickel(II), cobalt(II)

and cobalt(III) complexes

AUTHOR(S): Cros, Gerard; Gleizes, Alain; Laurent, Jean Pierre;

Darbieu, Marie Helene

CORPORATE SOURCE: Inst. Nat. Polytech., Univ. Paul Sabatier, Toulouse,

31077, Fr.

SOURCE: Inorganica Chimica Acta (1990), 174(1), 33-40

CODEN: ICHAA3; ISSN: 0020-1693

DOCUMENT TYPE: Journal LANGUAGE: English

N,N'-Bis(1-methyl-3-oxo-1-butenyl)oxamide (LH2) and N,N'-bis(1-methyl-3-oxo-1-butenyl)isophthalamide (L'H2) comprising amido groups adjacent to unsatd. fragments were synthesized. While reaction of metallic ions with L'H2 results in breaking of the imine bonds, defined complexes of ML (M = Cu, Ni, Co) and CoL(py)+ were isolated. CuL crystallizes as monoclinic, space group P21/c, a 8.862(2), b 16.014(2), c 9.105(1) Å,  $\beta$   $97.54(1)^{\circ}$ , Z = 4, R = 0.033, R' = 0.035. Intermol. Cu...O interactions lead to the formation of pseudo dimers. From the microanal. spectroscopic and magnetic data, polynuclear structures may be attributed to NiL.MeOH and CoL.3H2O whereas [CoL(py)2]ClO4 is likely a mononuclear species. The unexpected electrochem. behavior of these complexes points to a significant electronic transfer from the metal to the ligand resulting from the

presence of a large  $\pi$ -system. 36684-35-2P 132112-50-6P

RN 36684-35-2 CAPLUS

ΤT

CN Ethanediamide, N1, N2-bis(1-methyl-3-oxo-1-buten-1-yl)- (CA INDEX NAME)

RN 132112-50-6 CAPLUS

CN 1,3-Benzenedicarboxamide, N1,N3-bis(1-methyl-3-oxo-1-buten-1-yl)- (CA INDEX NAME)

L18 ANSWER 24 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

1957:87469 CAPLUS ACCESSION NUMBER:

DOCUMENT NUMBER: 51:87469

51:15859i,15860d-g ORIGINAL REFERENCE NO.:

Comparison of the effect of some antibiotics, TITLE:

antifungal substances, and phenylcarbamates on the

growth of two vascular parasites in vitro

Schneider, I. R. AUTHOR(S):

CORPORATE SOURCE: U.S. Dept. Agr., Beltsville, MD

SOURCE: Plant Disease Reporter (1957), 41, 436-41

CODEN: PLDRA4; ISSN: 0032-0811

DOCUMENT TYPE: Journal Unavailable LANGUAGE:

Agar disks containing laboratory cultures of the imperfect stages of the 2 vascular

parasites Ceratocystis ulmi and C. fagacearum were placed on agar plates (Difco PDA agar for C. ulmi and bran extract agar for C. fagacearum) which had the antibiotics, antifungal agents, and phenylcarbamates (which are plant growth regulators, rather than antifungal agents) to be tested incorporated in the agar. Most substances tested were about as effective against one organism as against the other. Exceptions were endomycin, fradicin, pleocidin, gramicidin S, and cycloheximide (antibiotics) and propynyl phenylcarbamate. C. ulmi was not significantly inhibited by 5 times the concentration of cycloheximide that completely prevented growth of C. fagacearum. Pleocidin was also more inhibitory to C. fagacearum, while gramicidin S, endomycin, fradicin, and propynyl phenylcarbamate were more inhibitory to C. ulmi. Most active against both organisms were endomycin, fradicin, fungichromin, ascosin, candicidin, several derivs. of 2-pyridinethio 1-oxide (Olin Mathieson 1562, 1564, 1456, and 1484), mycostatin, iso-Pr (chlorophenyl)carbamate, 1-carboxyethyl (3-chlorophenyl)carbamate, iso-Pr (3-chlorophenyl)carbamate, Et and phenylcarbamate, 2-chloro-1-methylethyl phenylcarbamate. Growth of the fungi on transfer to fresh media not containing the chems. showed the action to be usually fungistatic. Some of the 2-pyridinethiol 1-oxide derivs. and 2 phenylcarbamates were fungicidal, as was 25 times the min. inhibiting dose of cycloheximide.

1393-38-0, Subtilin ΤТ

(effect on vascular parasites)

RN 1393-38-0 CAPLUS

CN Subtilin (8CI, 9CI) (CA INDEX NAME)

\*\*\* STRUCTURE DIAGRAM IS NOT AVAILABLE \*\*\*

L18 ANSWER 25 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 1955:44866 CAPLUS

DOCUMENT NUMBER: 49:44866

ORIGINAL REFERENCE NO.: 49:8606h-i,8607a-h

TITLE: Green substantive anthraquinone dyes

PATENT ASSIGNEE(S): Sandoz Ltd.

SOURCE: Addn. to Brit. 692,513 (C.A. 49, 2082e)

DOCUMENT TYPE: Patent LANGUAGE: Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 713580		19540811	GB 1952-9958	19520421

GI For diagram(s), see printed CA Issue.

AB Green substantive anthraquinone dye mixts. are prepared by the method of the main patent by condensing a blue anthraquinone dye with a yellow azo dye by means of fumaroyl dichloride (I) or a substitution product thereof. The condensation product (II) 5.65 from 1-amino-4-bromo-2-anthraquinonesulfonic acid with 4,4'-diamino-biphenyl-3-sulfonic acid dissolved together with

p-(p-H2NC6H4N:N)C6H4SO3H (III) 2.8 in H2O 400 by means of 29% aqueous NaOH 4.8, the solution treated dropwise at 0-3° with I 1.6 while

maintaining the pH of the mixture at 4.5-5 by the simultaneous addition of 10% aqueous NaOH about 9, the mixture adjusted with 10% aqueous NaOH 2 to pH 7.5

and

salted with NaCl 12 parts, and the precipitate filtered in the cold and dried gave a green powder, green in H2O, which dyed cotton and regenerated cellulose fibers nice green tints of good light- and wash-fastness. This dye was separated by chromatog. into N-[4'-(4-amino-3-sulfo-1-amino-3-sulfoanthraquinonylamino)-2-sulfobiphenylyl]-N'-[4-(4-sulfophenylazo)phenyl] fumaramide (green component), N, N'-bis[4'-(4-amino-3-sulfo-1anthraquinonylamino)-2-sulfobiphenylyl]fumaramide (bluish green component), and N,N'-bis[4-(4-sulfophenylazo)phenyl]fumaramide. salt 5.8 of the condensation product from 1-amino-4-bromo-2,6-anthraquinonedisulfonic acid with (p-H2NC6H4)2 and the Li salt 2.85 of III in H2O about 500 treated dropwise at  $0-4^{\circ}$  with I 1.6 in CCl4 20 parts while maintaining the pH of the mixture at 5.8-6.2 gave similarly a green powder, yellowish green in H2O, which dyed yellowish green tints. II 6.1 and 4-(4-amino-2-methyl-phenylazo)azobenzene-3,4'-disulfonic acid (IV) 5.2 parts condensed as the Na salts in H20~600 at  $0-3^{\circ}$  with I 1.2 parts by volume gave a dark-green powder which dyed yellowish green tints. A similar dye was obtained with methylfumaroyl dichloride 1.3 parts. Chlorofumaroyl dichloride 1.3 or bromofumaroyl dichloride 1.4 parts gave similarly bluish-tinged green dyes of similar fastness properties. II 5.7 and 4-(4-amino-2-methylphenylazo)-3'-carboxy-2'-hydroxy-5'sulfobenzanilide (V) 4.75 dissolved with Li2CO30.9 in H2O 600 and treated at 0-3° with M maleic acid dichloride (VI) in CCl4 11 parts while maintaining the pH at 6.8 to 8 gave a dark-green powder which dyed green tints of good light- and wash-fastness. Aftertreatment of the dyeings with salts of Cu, Cr, Ni, Co, Fe, or Mn did not change the shade appreciably, but improved the fastness properties, especially the fastness to H2O. Coppering also improved the light-fastness. Maleic anhydride heated with PCl5, the POCl3 distilled off, and the residue of I and VI fractionated gave the desired VI. 1-Amino-4-(4-aminoanilino)-2-anthraquinonesulfonicacid (VII) 4.1 and 2-(4-amino-2-acetamidophenylazo)-4,8naphthalenedisulfonic acid  $4.7~\mathrm{parts}$  gave with I  $0.4~\mathrm{part}$  a dark powder which dyed full-green shades. Similar dyes were prepared in this manner by coupling by means of I the following components (shade of dyeing of the

ΙT

CN

resulting dye on cotton and regenerated cellulose fiber given): VII 4.1, IV 5.2, green; di-Na 1-amino-4-(p-aminoanilino)-2,6anthraquinonedisulfonate 5.35, Na salt of N-(p-aminobenzoyl) derivative (VIII) of IV 6.9, yellowish green; VII 4.1, VIII 6.0, full-green; VII 8.2, III 5.6, pure-green; II 6.1, 4-amino-3,2'-dimethylazobenzene-4'-sulfonic acid (IX) 3.3, vivid-green; VII 4.1, 1-(p-amino-phenyl)-3-methyl-4-(2-carboxy-4sulfophenylazo)-5-hydroxypyrazole (X) 4.2, pure-green; II 5.7, X 4.2, pure-green; II 5.7, 4-amino-3'-carboxy-4'-hydroxyazobenzene (XI) 3.1 yellow-tinged green (aftertreated with Cu, Ni, Co, Cr, Mn, and Al salts the shade was shifted slightly towards yellow); VII 4.1, XI 3.1, yellowish green; VII 4.1, XII 7.4, yellow-tinged green; mixed 1-amino-4-(4'-aminobiphenylamino)-2,5- and 2,8-anthraquinonedisulfonic acid (XIII) 5.7, XII 7.4, yellow-tinged green; XIII 5.7, 6,7-di-Cl derivative of II 6.4, yellowish green; XIII 5.7, 7-Cl derivative of II 6.1, yellowish green; XIII 5.7, 7-Br derivative of II 6.5, yellowish green; 1-amino-4-(4-amino-x-methoxyanilino)-2-anthraquinone-sulfonic acid (XIV) 4.5, X 4.2, green; x-Me analog of XIV 4.3, X 4.2, bluish green; VII 4.1, V 4.7, green; and VII 4.1, IX 3.05, green. 859335-69-6, 2-Anthraquinonesulfonic acid, 1-amino-4-[3'-sulfo-N'-[3-p-(psulfophenylazo)phenylcarbamoyl]acryloyl]benzidino]-(in dye mixture) 859335-69-6 CAPLUS

2-Anthracenesulfonic acid, 1-amino-9,10-dihydro-9,10-dioxo-4-[[4'-[[1-oxo-

3-[[4-[2-(4-sulfophenyl)diazenyl]benzoyl]amino]-2-propen-1-yl]amino]-3'-

sulfo[1,1'-biphenyl]-4-yl]amino]- (CA INDEX NAME)

PAGE 1-A

PAGE 2-A

PAGE 3-A

|| | O NH2

L18 ANSWER 26 OF 26 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 1922:6195 CAPLUS

DOCUMENT NUMBER: 16:6195

ORIGINAL REFERENCE NO.: 16:1079f-i,1080a-i

TITLE: Oxalic acid derivatives of "diacetonitrile"

AUTHOR(S): Benary, E.; Schmidt, M.

SOURCE: Berichte der Deutschen Chemischen Gesellschaft

[Abteilung] B: Abhandlungen (1921), 54B, 2157-68

CODEN: BDCBAD; ISSN: 0365-9488

DOCUMENT TYPE: Journal LANGUAGE: Unavailable GI For diagram(s), see printed CA Issue.

AB The work on MeC(NH2):CHCO2Et (A) (C. A. 11, 2786) showed that treatment with acid chlorides in C6H5N gives C- or N-derivs., depending on the nature of the chloride, while the Na derivative of A with esters always gives only N-derivs. The investigation has been extended to "diacetonitrile," MeC(NH2):CHCN (B), to determine the influence of a CN instead of a CO2Et group on the introduction of acid residues. E. v. Meyer believed that the products obtained by the condensation of "dinitriles" with esters in the presence of NaOEt or KOEt are all C-derivs. (C. A. 8, 3045) and as this is contrary to B.'s results, v. M.'s work has been repeated. The product of the condensation of B with (CO2Et)2 in the presence of NaOEt is really, as

was thought probable by Fleischhauer (J. prakt. Chemical 47, 391(1893)), the N-derivative, N-ethoxalyldiacetonitrile, MeC(NHCOCO2Et):CHCN (C), for with PhNHNH2 it yields a phenylhydrazide, MeC(NHCOCONHNHPh): CHCN (D), which is decomposed by acids into PhNHNHCOCONH2. On the other hand, with C1COCO2Et in C5H5N, B gives the C-derivative, MeC(NH2):C(CN)COCO2Et (E), which with 2 mols. PhNHNH2 gives H2O, NH3, EtOH and  $1-phenyl-3-methyl-4-cyanopyrazole-5-carbox-N\beta-phenyl-hydrazide$  (F), PhN·N:CMe·C(CN):CCONHNHPh, which reduces Fehling solution but does not split off PhNHNH2 by the usual methods; alkalies convert the CN into a CO2H group, giving an acid (G) identical with that obtained earlier by saponification of the product resulting from the action of PhNHNH2 on MeC(NH2):C(COCO2Et)CO2Et (H) but whose structure had not been determined With KMnO4 in Me2CO, F gives 1-phenyl-3-methyl-4-cyanopyrazole-5-carboxylic acid (I), which is saponified to the known 4.5-(CO2H)2 compound The product m. 147° earlier obtained from H and PhNHNH2 was therefore ethyl 1-phenyl-3-methylpyrazole-5-carboxphenylkydrazide-4-carboxylate. Attempted saponification of E with alkalies does not give the expected acid

(J);

there is considerable cleavage to NH3 and (CO2H)2. Concentrated HCl yields a substance (K) which has the composition of J but which shows no acid properties. As it seemed probable that J, first formed, isomerized under the influence of the coned. acid, MeC(NH2):C(CN)COCONH2 (L) was boiled with H2O, which slowly converted it into the NH4 salt of J, from which the Cu salt was obtained by precipitation with Cu(OAc)2 and this with H2S gave the free J; J is an enol., giving an intense red color with FeCl3, and rearranges with extreme ease, on warming in H2O, into the neutral K, MeC(:NH)CH·C(:NH)·O·O·CO; conversely, K allowed to stand some time with dilute NH4CH changes into J, while NaOH splits off NH3 and (CO2H)2. D, yellowish needles from alc., m. 192° (gas evolution), gives a violet color in concentrated H2SO4 with FeCl3, reduces hot Fehling solution C-Ethoxalyldiaceto-nitrile (E), long needles from EtOH-H2O, m.  $114-5^{\circ}$ , stable when pure but quickly decomps. if contaminated with adhering C5H5N (yield, 66%), gives no color in alc. with FeCl3, converted by alc. NH3 almost quant. into diacetonitrile-C-oxalamide (L), needles from H2O, begins to char 195°, decomps. into NH3 and (CO2H)2 on standing in N NaOH; anilide, from E and PhNH2 in alc., yellow leaflets from AcOH, chars 203-7°, gives an intense violet color with concentrated H2SO4 and K2Cr2O7, is unchanged by boiling 0.5 hr. with concentrated HCl. Diacetonitrile-C-oxalic imidolactone (K), best obtained (yield, above 60%) by shaking E a few min. with concentrated HCl, hexagonal pyramids from dilute AcOH, begins to char 230°, insol. in Na2CO3, soluble in NaOH with formation of NH3 and (CO2H)2 (if immediately acidified a part ppts. unchanged), soluble in aqueous NH4OH after several days without loss of (CO2H)2 and repptd. unchanged by HCl, can also be obtained from L with concentrated HCl, gives with PhNH2 in boiling dilute AcOH the

N-phenyl

derivative, golden yellow leaflets from AcOH, m. 236°, insol. in Na2CO3, gives no color in ale. with FeCl3. Diacetonitrile-C-oxalic acid (J), yellowish hygroscopic crystals from absolute alc., quickly deliquesces in the air; ammonium salt, quadrangular prisms with 1 H2O from H2O-EtOH, chars 180-220°; silver salt; copper salt, green. F (yield, about 72%), seps. from alc. in rectangular leaflets, m. 207°, gives a violet color in concentrated H2SO4 with FeCl3, reduces hot Fehling solution, converted by boiling 10% NaOH into 1-phenyl-3-methyl-pyrazole-5-carboxphenylhydrazide-4-carboxylic acid (G), needles from dilute alc., m. 253°, reduces hot Fehling solution I seps. from very dilute alc. in quadrangular prisms, m. 211-2° with loss of

CO2 and formation of 1-phenyl-3-methylpyrazole-4-nitrile, 4-sided prisms from MeOH, m. 193-4°. In the course of the present work was also prepared  $\beta$ -keto-butyronitrile-a-oxalamide diphenylhydrazone, MeC(:NNHPh)CH(CN)C(:NNHPh)-CONH2 (from L and PhNHNH2 in boiling alc.), long needles from alc., m. 232°, does not reduce Fehling solution, is unchanged by boiling with 50% AcOH or concentrated HCl. 1-Phenyl-3-methyl-4-cyanopyrazole-5-carboxanilide, from MeC(NH2):C(CN)COCONH-Ph and PhNHNH2 in boiling alc., needles from dilute alc., m. 167-8°, gives an intense violet color in coned. H2SO4 with K2Cr2O7, is not changed by boiling in AcOH with PhNHNH2. With PhNHNH2 in AcOH, both L and MeC(NH2):C(CN)COCONHPh yield F.

IT 1086248-71-6P

RL: SPN (Synthetic preparation); PRP (Properties); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent) (Oxalic acid derivatives of "diacetonitrile")

RN 1086248-71-6 CAPLUS

CN Acetic acid, 2-[[(1Z)-2-cyano-1-methylethenyl]amino]-2-oxo-, 2-phenylhydrazide (CA INDEX NAME)

Double bond geometry as shown.

IT 861801-85-6, Oxamic acid, N-( $\beta$ -cyano- $\alpha$ -methylvinyl)-(derivs.)

RN 861801-85-6 CAPLUS

CN Acetic acid, 2-[(2-cyano-1-methylethenyl)amino]-2-oxo- (CA INDEX NAME)

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